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Abstract

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Dissociation of Hexavalent Chromium from

Sanded Paint Particles into a Simulated Lung Fluid

Steven Harold Lange, Capt, USAF, BSC

Master of Science in Public Health, 2006

Thesis Directed By:

Peter T. LaPuma, Lt Col, USAF, BSC

Assistant Professor

Department of Preventive Medicine and Biometrics

Chromate-containing paint coatings are the primary means of protecting an aircraft surface from corrosion in the US military. Studies clearly link chromate exposure to human lung cancer. However, the few studies of the painting industry suggest that chromate exposure from paint particles does not increase the risk of lung cancer. Even fewer studies have evaluated sanding of chromate containing paint layers, and data suggests that sanders have an increased risk of lung cancer.

A 6-stage cascade impactor was used to imitate particle deposition onto a layer of lung fluid. The lung fluid was simulated with a porcine based mucin. Sanded particles were collected based on particle size into the impactor's six petri dishes, which contained lung fluid. After 24 hours, the fraction of chromate that dissolved into the lung fluid generally ranged from 60-90% for strontium chromate based paints and 10-50% for barium chromate based paints. In water and solvent based strontium chromate paints, there was little difference between sanded and freshly sprayed paint particles. But for polyurethane and barium chromate based paints, sanded particles dissociated significantly more chromate than paint particles.

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Dissociation of Hexavalent Chromium from Sanded Paint Particles into a Simulated Lung Fluid

By

Steven Harold Lange

Thesis submitted to the Faculty of the Department of
Preventive Medicine and Biometrics Graduate Program of the
Uniformed Services University of the Health Sciences in partial fulfillment
of the requirements for the degree of

Master of Science in Public Health 2006

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1 Introduction

1.1 Background

1.1.1 Hexavalent Chromium

The respiratory tract is the major target of hexavalent chromium (Cr⁺⁶) inhalation exposure (Williams, *et al.*, 2000). Cr⁺⁶ is a known lung carcinogen which causes deoxyribonucleic acid (DNA) mutation (IARC, 1990). When particles containing Cr⁺⁶ enter the lungs, they interact with the fluid in the lung. Cr⁺⁶ reduction to Cr⁺³ in the lung, and the creation of reactive intermediates, is believed to be the mechanism of Cr⁺⁶ carcinogenesis (Klaassen, 2001). In order to reach the DNA of the lung cells, the Cr⁺⁶ must dissociate from the host particle and diffuse through the lung fluid to reach the cell. This research was undertaken to determine how much Cr⁺⁶ dissociates from respirable particles generated by sanding aluminum test panels coated with chromate containing primers. This builds on, and compares previous work examining Cr⁺⁶ dissociated from particles generated by spraying chromate containing primers.

Cr⁺⁶ is extremely effective and widely used as a corrosion inhibitor for high-strength aluminum alloys in aerospace applications (Zhao, *et al.*, 2001). In its pure form, aluminum is soft, ductile and resistant to corrosion. Most commercial uses require greater strength than that of pure aluminum. Greater strength is achieved by the addition of other elements, thus producing aluminum alloys. Aluminum alloy 2024 (3.8 - 4.9% copper, 1.2 - 1.8% magnesium (MatWeb, 2006)) is perhaps the best known and most widely used aircraft alloy (Aluminum Association, 2006). However, the addition of

these impurities reduces the corrosion resistance of pure aluminum. Therefore, the aluminum alloy is protected through the use of Cr⁺⁶.

1.1.2 Regulation

Personal exposure to Cr⁺⁶ is heavily regulated. The Occupational Safety and Health Administration (OSHA) reviewed epidemiologic data from several industry sectors including chromate production, chromate pigment production, chromium plating, stainless steel welding, and ferrochromium production. The data was used as supporting evidence in a more stringent standard (OSHA, 2006).

OSHA's original permissible exposure limit (PEL) for workplace exposure to Cr⁺⁶ was a ceiling concentration of 52 ug/m³ as Cr⁺⁶. This limit, adopted in 1971, was based on a 1943 recommendation established to control irritation and damage to nasal tissues. The American Conference of Governmental Industrial Hygienists (ACGIH) first recommended control of workplace exposures to Cr⁺⁶ 1946, recommending a time-weighted average (TWA) Threshold Limit Value of 100 ug/m³ as Cr⁺⁶. ACGIH also classified certain Cr⁺⁶ compounds as class A1 (confirmed human) carcinogens in 1974 (OSHA, 2006).

In 1997, OSHA was sued for unreasonable delay in issuing a new Cr⁺⁶ standard. The court set deadlines of October 4, 2004 for publication of a proposed standard and January 18, 2006 for publication of a final standard. OSHA published the final standard on 28 February 2006. OSHA's ceiling limit of 52 ug/m³ (as Cr⁺⁶) was lowered to an 8 hour TWA of 5 ug/m³ (as Cr⁺⁶) for chromate compounds. In this new standard, OSHA made unique provisions for the aerospace industry by establishing a standard of 25 ug/m³ when painting aircraft or large aircraft parts, in conjunction with engineering and work

practice controls. However, OSHA has determined that sanding operations in the aerospace industry can control exposures through local exhaust ventilation at the source of exposure (vacuum sanders). Sanding operations are subject to the lower 5 ug/m³ standard. (OSHA, 2006)

1.1.3 Military Relevance

In 2004, the United States Air Force (USAF) conducted an analysis of corrosion control costs. This study covered aircraft, vehicles, equipment, munitions, and space systems. Costs were documented as those directly related to corrosion control such as maintenance, repair, treatment, washing, painting, depainting, and sealing. These costs were only for items that could be directly identified. It did not include any environmental, health or safety related costs. In 2004, the USAF spent almost \$1.5 billion, approximately 4% of its total Operations and Maintenance budget on corrosion control (Reed, 2004). In light of this, the military continues to study replacements for Cr⁺⁶. Currently, the principle and most versatile means of protecting metal surfaces is a coating system that will resist corrosion.

Aircraft surfaces are coated in various ways with a variety of materials to add to their ability to resist harsh environments. There is a multi-layer system used to protect metal surfaces of military aircraft, missiles, and aerospace ground equipment. It is well known that these coating systems provide a protective barrier against environmental degradation of the metal exterior. The layered coating system consists of a chromate conversion coating, a chromate containing primer, and topcoat. Cr⁺⁶ is the active ingredient in chromate conversion coatings and primer paints used to protect the metal skins of aircraft from corrosion processes.

Aluminum alloy aircraft skins are treated with a chromate conversion coating prior to priming and painting. As aircraft flex, stress fractures may form in the aluminum skin, exposing the metal to the air. This is a vulnerable site for oxidative damage. It has been shown that chromate is released from the coatings to bind with the exposed metal. Zhao *et al.* revealed that chromate released from chromate conversion coatings migrated to the nearby exposed aluminum alloy surface, providing corrosion resistance for the exposed surface (Zhao *et al.*, 2001). The chromate conversion coating is Cr⁺⁶ dissolved in nitric acid. This material is sprayed, immersed, or brushed onto the metal, allowed to dwell briefly, and rinsed or wiped off. The conversion coating leaves a thin protective film of Cr⁺⁶. The conversion coating provides corrosion resistance and provides better primer adhesion to the aluminum surface (NAEC, 1990; USAF, 2001).

The second layer is a chromate-containing primer. The Cr⁺⁶ used in primer paints typically is in the form of a chromate salt (bound to metals such as barium (Ba), strontium (Sr) and zinc (Zn)), and is a suspended solid within a paint matrix (LaPuma, *et al.*, 2002). Primer paints are sprayed onto the aluminum surface and allowed to cure. Besides better adhesion, the primer places an added layer of chromate on the surface as a reserve to protect the base metal. (Carlton, 2003a). Chromate-containing primers out perform non-chromate alternatives (LaPuma, *et al.*, 2001). The primer provides a reaction site for the topcoat; the solvents and binders in the topcoat react with the primer (USAF, 2001).

The final coating is the topcoat. The topcoat aids in achieving optimal protection by providing an additional barrier. This coating can be polyurethane, enamel, lacquer, varnish, or other heavy elastomeric materials. The topcoat is selected based on the environment to which the surface will be subjected. The combination of these three coatings ensures protection of the aluminum surfaces.

It is necessary to have a properly prepared surface to apply these coatings to achieve maximum corrosion protection. During aircraft repair or maintenance, workers mechanically remove existing coatings with hand-held sanders or blasting with abrasive media. The particles generated during mechanical sanding of aircraft often will contain chromate. Two studies were published where air samples were collected to determine chromate concentrations during mechanical paint removal in aerospace applications. The upper confidence limits for the Cr⁺⁶ TWA exposures documented in these studies (6.4 and 12.0 ug/m³) exceeded the new OSHA standard of 5 ug/m³ (Carlton, 2003a, 2003b).

Research is ongoing to find a suitable replacement for chromate coatings partly due to regulatory pressure. In 1997, the Department of Defense Joint Group on Pollution Prevention (JGPP) investigated non-chromate primers to replace the chromate primers now in use. After lab testing, two non-chromate primers are currently being evaluated on operational aircraft (JGPP, 1998). A second study of non-chromate primers started in 2006 (JGPP, 2006). The more stringent permissible exposure limits will make compliance difficult in military corrosion control facilities.

1.1.4 Lung Cancer Incidence

Because chromate causes cancer through DNA mutation, if a particle is inhaled, the chromate needs to separate from that particle, dissolve into the mucosal layer, cross the cell membrane and reach the DNA. In the tracheobronchial region, inhaled particles are trapped in the mucosal fluid and removed from the lung via the mucociliary escalator. The majority of particles are removed within 24 hours. The mucosal fluid along with the

trapped particles, are then deposited into the gastrointestinal (GI) tract, which is not considered to be a significant pathway of concern for Cr⁺⁶ (Proctor, *et al.*, 2002). In order to cause cancer, Cr⁺⁶ must reach the DNA of the lung tissue. To do this, Cr⁺⁶ must dissociate from a sanded paint particle into the mucosal fluid and be transported into the cells of the lung tissue, as illustrated in Figure 1-1.

Conceptual Diagram of Chromate Transport Pathway

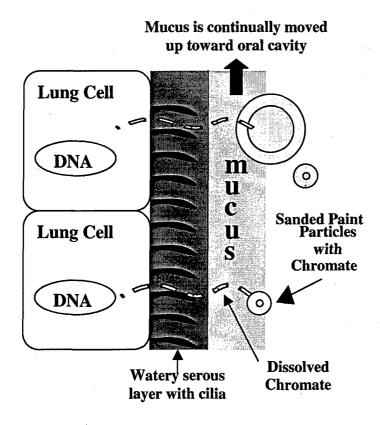


Figure 1-1: Dissociation of Chromate in Mucus (Moran, 2005)

Many factors may affect the amount of chemical released from a particle into the mucosal fluid such as particle size, chemical solubility, and interaction with proteins/mucins. If a fraction of a chemical dissociates from a particle, for example 10%, into the surrounding lung fluid, the dose to the lung tissue is only 10% of the total mass inhaled. If another type of particle releases 100% of the total mass inhaled, then the dose

to the lung tissue is 10 times higher than the particle that only releases 10%. A method to measure the fraction of a chemical that dissociates from particles into lung fluid will be used in this study to determine chromate dissociation from sanded paint particles.

(Moran, 2005)

Most of the epidemiological and risk assessment data for Cr⁺⁶ comes from industries other than painting such as chromate pigment production, welding, leather tanning and Cr plating industries (OSHA, 2006). These industries have well-documented data showing a clear link between exposure and lung cancer. However, this is not the case for the painting industry. There have been relatively few epidemiological studies of painters using chromate containing paints, and even fewer studies on sanding of chromate-containing coatings and lung cancer. The few painting and sanding studies do not break out different tasks, and painters often do varying amounts of sanding to prepare surfaces for painting.

1.1.5 Simulated Lung Fluid

Particulate testing on animals is costly and difficult because of differences in lung physiology between animals and humans and the difficulty in consistently generating particles that mimic sanding operations. In this study, sanded paint particles will be collected into a porcine-based simulated lung fluid (Porcine-SLF) to determine the mass of Cr⁺⁶ that dissociates from the particulates. Using a cascade impactor, sanded paint particulates will be collected and separated based on particle size into petri dishes containing the Porcine-SLF.

Collecting these particles directly into Porcine-SLF provides a more realistic simulation of particles being trapped into lung fluid. The dissociation of chromate into

the lung fluids will be influenced by the particle surface and lung fluid interaction. There are also influences caused by different particle sizes such as the surface to volume ratio and the amount of paint surrounding the chromates.

1.2 Research Questions and Specific Aims

This study was designed to answer the following questions:

- 1. Does particle size have an effect on the amount of Cr⁺⁶ that dissociates from a sanded paint particle?
 - **Specific Aim:** Collect sanded paint particles of various size and compare the fractional release of Cr⁺⁶ into a SLF over a 24-hour period for each of six different particle size ranges (total range from 0.65 to 7+ um).
- 2. Does the type of paint have an effect on the amount of Cr⁺⁶ that dissociates from a sanded paint particle?
 - **Specific Aim:** Measure the difference in the fractional release rate of Cr⁺⁶ as a function of particle size for four military types.
- 3. Does the amount of Cr⁺⁶ that dissociates from spray painting particles differ from the amount of Cr⁺⁶ that dissociates from sanding primer paint coatings?
 - **Specific Aim:** Determine the fraction of Cr⁺⁶ released from particles generated by a sanding operation into a SLF over a 24-hour period and compare to the release rate of particles generated from a spray painting operation.

2 Literature Review

2.1 Overview

This research is designed to study whether the release rate of chromate from different types of paint particles have different chromate release rates into a lung fluid. Regulators are influenced by epidemiology studies that focus primarily on chromate production and pigment production industries. Few epidemiology studies have focused on the painting or sanding industry. This chapter discusses the composition of tracheobronchial lung fluid secretions and the role of lung fluid in mucociliary clearance. This chapter also will provide an overview of the epidemiological studies involving chromate. Finally, the viable cascade impactor and how it captures and separates inhalable particles into Porcine-SLF will be discussed in this chapter.

2.2 Mucociliary Clearance

The lungs are continuously exposed to ambient air that contains particles. An effective cleaning system in the lung's upper airways is called mucociliary clearance. Mucus lines the upper airways and traps particles that may enter. Ciliated epithelium lines the respiratory system from the trachea to the terminal bronchioles. The length of cilia is approximately 6 um in the trachea, and 3.6 um in the bronchioles, with both having a diameter between 0.1 – 0.2 um (Wanner, *et al.*, 1996). The cilia rhythmically move airway mucus up and out of the lungs where the majority of the mucus and particles are swallowed into the digestive system (Servera, *et al.*, 2003). The main function of the mucociliary apparatus is to keep particles out of the deeper region of the lungs to protect the alveoli. The mucus layer is a mechanical barrier for particles and

bacteria and it also contains antioxidant properties (Thornton & Sheehan, 2004; Wanner, et al., 1996).

Mucociliary clearance occurs in two phases, initial (or fast) and slow. Initially, trapped particles are removed by the mucociliary apparatus. Mucus velocity rates in the tracheobronchial tree vary considerably. Studies indicate particles should be removed between 2.5 and 24 hours in healthy, non-smoking adults (Agnew, 1991; Ilowite, *et al.*, 1989; Lippmann & Schlesinger, 1984; Smaldone, *et al.*, 1988). The slow phase may take weeks to months to remove particles. This phase removes particles that have traveled deep into the lung's alveolar region and are removed by phagocyte cells or dissolution in the lungs (Brain, *et al.*, 1994; Jones, 1984).

2.3 Human Lung Fluid (Mucus)

The airway surface liquid has two separate layers of fluid. The combined depth of both layers varies from 5-10 um depending on its location in the respiratory tract. These two layers are called the periciliary sol layer and the mucus gel layer. The depth of the sol layer is assumed to be equivalent to the average height of the epithelial cilia (Widdicombe, 2002). The mucus gel layer floats on top of the sol layer. The tips of the beating cilia interact with the overlying mucus gel layer, which carries the mucus out of the lungs to the oral cavity where it is swallowed into the digestive system. In healthy individuals, mucus moves approximately 4-5 mm per minute (Yeates, *et al.*, 1975). In the same way, the nasal passage traps and removes particles via mucociliary clearance. The nasal cilia transports mucus to the back of the throat where it is swallowed (Davidson, 2003).

The mucus layer consists mainly of water bound in a viscoelastic gel containing mucins. Mucins are large glycoproteins rich in carbohydrates. Mucins vary in size, ranging from 3 million to 32 million Daltons (Kim, et al., 2005). Mucins consist of a protein core with oligosaccharide side chains. These molecules form a self-associating link end to end forming very long chains. It is believed these associations are carbohydrate-protein or carbohydrate-carbohydrate interactions forming a gel-like material (Hill, et al., 1977). The proteins resemble a "bottle brush with straight peptide backbone, bristle-like oligosaccharide chains radiating from the core, and a non-glycosylated handle" (Boat & Cheng, 1980). These 'brushes' aggregate through the interactions listed previously, forming a gel matrix. This contributes to the viscoelasticity of the mucus that can be stretched to long distances without breaking (King & Zayas, 2004).

Mucin enters the airways from two different locations: airway epithelial cells and submucosal glands (Nadel, et al., 1979). Mucin can exist in a condensed or an expanded phase. Mucin is produced and maintained in the cell in the condensed phase (granules). Once secreted into the airways, the condensed mucin becomes hydrated and its volume rapidly expands several hundred times (Kim, et al., 2005; Wanner, et al., 1996). The expanded mucus floats on the periciliary sol layer and can no longer penetrate between the cilia (Widdicombe, 2002).

Gastric based pig mucin (Porcine-SLF) was used to simulate human lung fluid in this study. Human lung fluid is a very complex mixture and difficult to obtain. Porcine-SLF can be produced from readily available materials and it has viscoelastic properties

similar to human mucus. The Porcine-SLF used in this study was prepared in the method reported by List, *et al.* (List, *et al.*, 1978), and is discussed in more detail in Chapter 3.

2.4 Bioavailability

2.4.1 Particle Size

The size of sanded paint particles can affect the bioavailability of particles in a variety of ways. During sanding, particles are sheared from the metal surface with an abrasive material. The sheared particulates come off the surface in varying size. Several studies demonstrate that smaller particles contained disproportionately less Cr⁺⁶ per mass of dry paint than larger particles for three common chromate containing aircraft primers (LaPuma, *et al.*, 2001; Novy, 2001; Rhodes, 2002). Also, a study on Cr⁺⁶ dissociation from four primer paints during spray painting suggests that Cr⁺⁶ dissociates faster from smaller paint particles (Schilke, 2002).

2.4.2 Solubility

The solubility of a solid or liquid also affects its bioavailability. In order for a solid to dissolve into surrounding liquid, the concentration in the fluid must be less than the saturation concentration. For Cr⁺⁶ to dissociate from a sanded paint particle, the lung fluid surrounding it must be below the saturation concentration of the chromate.

Saturation of strontium chromate in water is 1200 ppm (Weast, *et al.*, 1985). Saturation of strontium chromate in Porcine-SLF is 35 ppm, which will be discussed in chapter 3.

2.4.3 Residence Time

The length of time a particle is in contact with lung fluid may affect the amount of chromate that can dissociate into the lung fluid. Three studies investigated the effect of residence time on the dissociation rate of chromate (Kauth, 2001; Morgan, 2000; Novy,

2001). Each found that paint particles release most of their chromate within the first 24 hours. Studies have demonstrated that mean retention time of particles in the upper tracheobronchial region in the lungs is 24 hours (Albert, et al., 1973; Camner, et al., 1997; Ilowite, et al., 1989; Smaldone et al., 1988). More recent studies have shown that retention time in the lungs is also dependent on particle size. Particles 6 um and larger generally are cleared from the tracheobronchial region of the lungs in 24 hours, while the fraction remaining increases as particle size decreases from 6 um. These smaller particles are cleared through a combination of both slow and fast clearance. Möller et al reports that half of the 2 um particles entering the lungs will be removed in 24 hours, and the remaining particles will be completely removed approximately 110 days later (Moller, et al., 2006). The higher fraction of retained particles is most likely due to a higher percentage reaching the alveolar region of the lungs where mucociliary clearance is not present. A 24 hour residence time was used for this study, which parallels the time required for most particles to be carried out of the tracheobronchial region of the lung via the fast clearance of the mucociliary escalator mechanism.

2.4.4 Paint Matrix

The physical and chemical characteristics of paint particles vary depending on the type of paint and how they are used. The interaction between the paint type (solvent, water, or polyurethane), physical state (wet, dry), chemical constituents and the chromate compound type (Sr, Ba) differ between paint types and potentially affect the rate of Cr⁺⁶ dissociation. Sprayed paint particles enter the respiratory system wet, while sanded particles are generated by abrasion and enter the respiratory system dry. Therefore, the characteristics of dry sanded paint particles are expected to interact with lung fluids

differently than wet sprayed paint. Also, the different type of paint is likely to influence dissociation of Cr⁺⁶ in lung fluid.

Previous work investigating dissociation of four sprayed primer paints indicates solvent and water based strontium chromate (SrCrO₄) paints have no significant difference in overall Cr⁺⁶ dissociation. However, polyurethane SrCrO₄ paint dissociates significantly less Cr⁺⁶ than solvent and water based paints. Dissociation of Cr⁺⁶ in water-based barium chromate (BaCrO₄) is significantly less than the SrCrO₄ paints (Moran, 2005). Sprayed paint may be tacky when entering the lungs and therefore may stick to the mucus layer better than a sanded particle. A spray paint particle is more likely to have the chromate salt encapsulated by the paint matrix. However, sanding will tear the painted surface, potentially exposing the Cr⁺⁶.

2.5 Health Effects

2.5.1 Overview

The primary health effect from Cr⁺⁶ is lung cancer, although it is also known to cause asthma and perforation to the nasal epithelia and skin (OSHA, 2006).

Epidemiological studies have clearly linked Cr⁺⁶ exposures to lung cancer in several industries. However, there are three studies indicating painters using paints containing Cr⁺⁶ do not have an increased risk of lung cancer (Alexander, *et al.*, 1996; Boice, *et al.*, 1999; Dalager, *et al.*, 1980). Further, fewer studies break down tasks of painters, such as sanding surfaces prior to painting. One aerospace industry named sanding tasks as a separate category and suggests there may be a higher risk of lung cancer in sanders, but the results were inconclusive. The following section will briefly discuss epidemiology studies in the chromate production and the chromate pigment production industries that

reveal an increased risk of lung cancer. Followed by a discussion of the studies on the painting and sanding industry. Table 2-1 summarizes the relevant epidemiology studies.

2.5.2 Chromate Production Industry

The mortality of workers in chromate production plants located in Baltimore, Maryland (Gibb, et al., 2000; Hayes, et al., 1979), and Painesville, Ohio (Luippold, et al., 2003; Mancuso, 1997) have been studied multiple times. Hayes et al. investigated whether changes in production were associated with reduced risk, and whether excess risk could be associated with length of exposure or production area. He retrospectively examined 1,803 male workers who were employed between 1945 and 1974. Each was exposed at least three months to sodium chromate and dichromate salts from three production departments: milling (dust particles), dichromate (mists), and special products (chromic acid mists). In 1950, the plant added a new production facility with process improvements to minimize workers' exposure. Their health status was evaluated in 1977. The Hayes study incorporated exposures from both the old and new facilities. He reported an overall ratio of observed to expected (O/E) cancer risk of the trachea, bronchus, and lung of 2.0 (p<0.01).

Gibb *et al.* also retrospectively assessed a cohort of 2,357 male workers at the same Baltimore plant studied by Hayes, but included only those workers who began work in 1950 when the new plant construction was completed. The employees worked between 1950 and 1974, and their health status evaluated in 1992. Gibb reported an overall cancer of the lung O/E of 1.80 (95% CI 1.49 to 2.14). Both studies found increased cancer with increased length of exposure. Both studies incorporated age adjusted data, however, only Gibb was able to adjust for smoking.

Incomate Type Smoking Age Adj. Lung Cancer O/E (95% CD)) Comments	Chromate Production	Iium Chromate N Y 2.0 Increased lung cancer risk with increased duration of employment	N Y Not Listed Increa	Y Y 1.86 (1.49-2.14) Increased mortali	lium Chromate N Y 2.41 (1.80-3.17) Increased mortality with increased exposure	Chromate Pigment Production	VZinc Chromate Y Y A4 Observed Lung Cancer: 6, Expected 0.135	N V Increased mo		VZinc Chromate N Y 3.6 (2.13-5.68) Increased mortality with increased exposure	Painting Operations	inc Chromate N Y 1.84 Appears to be elevated lung cancer risk	pecific Chromate N Y 1.425 No statistical significance Pigments	c, Strontium & N Y 1.1 (0.5-2.0) Lung cancer risk did not increase with ad Chromates exposure	N Y 2.7 (0.5-7.8) Only among thos	pecific Chromate N Y 1.11 (0.8-1.51) No increase in lung cancer risk	N 1.4 (1.2-1.7) Increas	1.5° (1.0-2.1) duration of employment
		2.0	Not Listed	1.86 (1.49-2.1	2.41 (1.80-3.1′	tion	4	1.97	$1.02^2 (0.56-1.7)$	3.6 (2.13-5.68		1.84	1.425	1.1 (0.5-2.0)	2.7 (0.5-7.8)	1.11 (0.8-1.51	1.4 (1.2-1.7)	$1.5^{\circ}(1.0-2.1)$
Age Adj.	uction	> -	¥	Y	7	Produc	*	>	•	Y	tions	7	¥	>	7	>	z	
Smoking Adj.	omate Prod	Z	Z	Ā	Z	te Pigment	Y	Z		Z	inting Opera	Z	z	Z	Z	Z	Z	
Chromate Type	Chr	Sodium Chromate	Sodium Chromate Calcium Chromate	Sodium Chromate	Sodium Chromate Calcium Chromate	Chroma	Lead/Zinc Chromate	Sodium Chromate	Calcium Chromate	Lead/Zinc Chromate	Pai	Zinc Chromate	Non-Specific Chromate Pigments	Zinc, Strontium & Lead Chromates	Zinc, Strontium & Lead Chromates	Non-Specific Chromate Primers/Paints	Lead/Zinc Chromates	
Population of Workers		1803 Males	332 Male	2357 Male	493 Unspecified		133 Male	2298 Male		294 Male		977 Male Painters	226 Male Auto. Painters	1.064 Aerospace Painters	877 Aerospace Sanders	1216 Painters	10,428 Male	Lacyucieis
Study Type ¹		P & RCC	RC	RC	RC		RC	RC		RC		RC	RCC	RC	н	RC	RC	
Author		Hayes 1979	Mancuso 1997	Gibb 2000	Luippold 2003		Langard 1983	Davies 1991		Deschamps 1995		Dalager 1980	Chaizze 1980	Alexander 1996	=	Boice 1999	Brown 2002	

Notes: ¹ Study Type: P is Prospective, RC is Retrospective Cohort, RCC is Retrospective Case Control ² New Facility Data ³ Workers working through two census periods

Table 2-1: Summary of Relevant Epidemiology Studies

Similar results were found at the Painesville, OH, chromate production plant.

Luippold *et al.* retrospectively evaluated 482 male employees who worked from 1941 through 1997. The trachea/bronchus/lung cancer O/E was 2.41 (95% CI 1.80 - 3.17).

Mancuso *et al.* retrospectively reviewed a cohort of 332 workers through 1993. These workers were employed at the same Ohio production plant. He observed an increasing lung cancer death rate with increasing exposure to Cr. While neither study was able to correct for smoking, age adjustments were made.

2.5.3 Chromate Pigment Production Industry

Pigment production plants generate pigments containing chromates. Workers may be exposed to these chromates in the form of dusts. Workers generally have higher exposures to dusts created during the milling process and moderate exposures from the washing and drying processes. Davies *et al.* (Davies, *et al.*, 1991) retrospectively studied a cohort of 1,422 men exposed to calcium and sodium chromate at two large chromate production factories in Britain. An overall lung cancer O/E of 1.97 (p<0.01) was observed. The cancer rate was higher among the workers exposed to higher chromate levels (O/E of 2.45 versus 1.07 among men in jobs with less Cr⁺⁶ exposure). Davies also reports that after a new facility went into use, when no significant risk of lung cancer existed, reporting an O/E of 1.02 (95% CI 0.56-1.71).

Deschamps *et al.* (Deschamps, *et al.*, 1995) also studied the chromate pigment industry with a retrospective cohort of 294 men. In this group, Deschamp found a lung cancer O/E of 3.60 (95% CI 2.13 - 5.68). A significantly higher rate of lung cancer was found for workers who were employed 10 years or more.

In addition, Langard *et al.* (Langard & Vigander, 1983) retrospectively analyzed a small cohort of 133 workers in the zinc chromate pigments production industry. Similar to the chromate production studies, increased chromate exposure resulted in increased lung cancer. Langard found a lung cancer O/E of 44, based on 6 observed cases and 0.135 expected cases. Langard was able to correct for smoking.

In both the chromate production and chromate pigment production studies, it was evident that increased lung cancer and/or lung cancer mortality existed for those exposed to the highest concentrations, and those exposed for the longest times.

2.5.4 Painting Industry

Few epidemiological studies have been conducted on painters using paints containing chromates. Alexander *et al.* (Alexander *et al.*, 1996) retrospectively studied 2426 aerospace workers employed between 1974 and 1994. The workers had a minimum of six months of employment. Alexander broke down the workers into sub-groups; among them were spray painters, and maskers/sanders. Estimates of lung cancer risk were based on length of employment, and industrial hygiene exposure data. The overall lung cancer O/E was 0.8 (95% CI 0.4 - 1.3). The lung cancer O/E for the 1064 spray painters was 1.1 (95% CI 0.5-2.0), and the lung cancer O/E for the 877 sanders was 0.7 (95% CI 0.3-1.3). However, when separating the sanders who worked at least 5 years as a sander, the lung cancer O/E was 2.7 (95% CI 0.5 - 7.8), based on three cases. Alexander theorized the difference between cancer rates in sanders (2.7) versus painters (0.8) may be the proportion of respirable particles in the dust versus painting mist. Alexander's cohort was small, lacked smoking data, and had a young population.

Boice et al. (Boice, et al., 1999) studied a retrospective cohort of 77,965 aircraft manufacturing workers who were employed after January 1, 1960, and worked at least one year. No evidence of increased lung cancer was found. The study included 1216 painters, for which the lung cancer O/E was reported as 1.11 (95% CI 0.8-1.51). Job families were formed using job codes and job titles. Exposure assessments were based on worker interviews and walk-through surveys. Boice's cohort lacked smoking data, but was corrected for age.

Dalager et al. (Dalager, et al., 1980) retrospectively studied 977 male spray painters at government owned aircraft maintenance facilities who worked at least three months and terminated their employment prior to July 31, 1959. The painters used paints containing zinc chromate. Dalager observed an excess respiratory cancer (21 observed, 11.4 expected) among 'painters', with a respiratory cancer O/E of 1.84 (p<0.01). In her discussion, Dalager mentions that, "metal surfaces were prepared for painting by painters' helpers." Therefore, the observed excess cancer risk includes sanders. The study also did not correct for smoking, which is more prevalent among painters (Friedman, et al., 1973).

Chiazze et al. (Chiazze, et al., 1980) conducted a case control study of painters exposed to chromate containing primers and paints in the automotive industry whose job title was associated with spray painting. The cohort consisted of 226 painters at ten manufacturing plants from five companies. The cohort studied consisted of workers who died between 1970 and 1976. The lung cancer O/E was 1.425; but statistical significance was not achieved. This study did not correct for smoking. OSHA did not include the

Chiazze study as Supporting Evidence for the Occupational Exposure to Hexavalent Chromium, Final Rule (OSHA, 2006).

Brown *et al.* (Brown, *et al.*, 2002) studied the risk of cancer among men and women in the painting trades in Sweden from their 1960 and 1970 census. One group evaluated was a cohort of 10,428 male lacquerers exposed to lead and zinc chromates. She observed a lung cancer O/E of 1.3 (95% CI 1.1 - 1.6). For lacquerers working during both censuses, the O/E increased to 1.5 (95% CI 1.0 - 2.1). Brown mentions these workers were exposed to high levels of paint dust containing lead and zinc chromates. High levels of dust may be due to sanding old layers of chromate primers. Brown's data was not adjusted for smoking.

Terstegge *et al.* (Terstegge, *et al.*, 1995) studied mortality patterns of commercial painters in the Netherlands. The study population consisted of 9,812 painters who had died between 1980 and 1992. An increased risk of lung cancer in painters was reported. The authors believe sanding down old paint layers may expose painters to chromates. Neither the Brown nor Terstegge study was mentioned in OSHA's Final Rule.

The studies of Cr production and pigment production plants comprise workers who were exposed to chromates as dust particles. Studies of painters suggest increased cancer risk among sanders. Sanded paint particles may pose a higher risk of lung cancer than the types of particles generated from painting. It is possible that the Cr⁺⁶ in a sanded paint particle interacts with the lung fluid in a manner similar to particles generated in the chromate production and pigment industries.

2.6 Particle Collection

2.6.1 Overview

Particle size, shape, density, and hygroscopicity determine how the particle will behave in air, how efficiently they are deposited in the respiratory system, and how they interact within the lung (DiNardi, 1998). Most particles created in sanding are not spherical or uniform. A particle will deposit within the human lung based on its aerodynamic diameter and not by its physical dimensions (Wells, 1955). To determine Cr⁺⁶ dissociation among different sized particles, a collection device must be used to separate particles into different size ranges. In this study, viable cascade impactors were used to separate particles into size ranges and deposit them into the Porcine-SLF.

2.6.2 Cascade Impactors

Cascade impactors operate under the principle of inertia. Airflow changes direction inside a cascade impactor, as illustrated in Figure 2-1. Larger particles with inertia will not turn as readily as smaller particles and will impact the flat surface. Smaller particles with less inertia will continue to flow through the impactor toward the lower stages. In the lower stages, the jets continue to get smaller, and the air velocity increases.

Consequently, smaller particles cascade onto the lower stages based on their inertia.

In 1956, Andersen designed a viable cascade impactor consisting of six stages in series. Each stage has a plate with 400 holes, and below it a petri dish with culture medium, Figure 2-2. Air is drawn through the impactor at a constant rate of 1 cubic foot per minute (CFM) with a vacuum pump. Andersen's design evenly distributes the air across the surface of the petri dish. Andersen also discovered electrostatic charges from plastic petri dishes reduced collection efficiency by about 20 percent, and aluminum

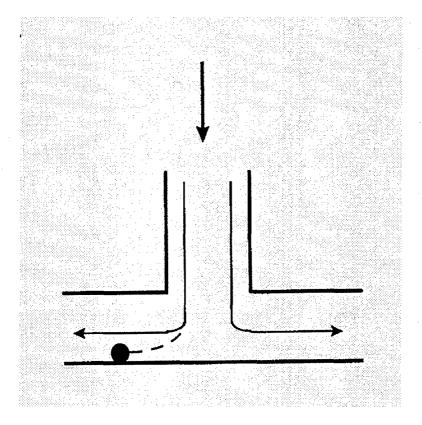


Figure 2-1: Particle Impaction Theory (DiNardi, 1998)

dishes hindered observation. Therefore, glass petri dishes are generally used in viable cascade impactors. In addition, Andersen ran experiments to determine the optimum amount of sample medium that should be placed in the petri dish; 27 mL was found to be the most advantageous amount of medium (Andersen, 1958).

A six-stage viable cascade impactor from Tisch Environmental (TE-10-800) was used in this study. This impactor is based on Andersen's design. The jet diameters run from 1.18 mm on the first stage to 0.25 mm on the last stage. The large number of jets minimizes turbulent flow, reduces dead space and results in sharp cutoffs between stages. Table 2-2 lists each stage, jet diameter, and the particle sizes each stage collects.

Cascade impactors are widely used today. For example, impactors are prevalent in the pharmaceutical industry, typically used in particle size analysis of aerosols from

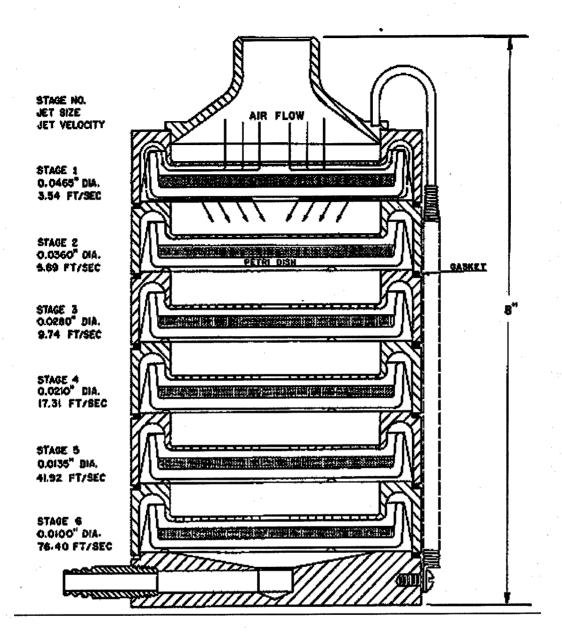


Figure 2-2: Six Stage Andersen Cascade Impactor (Andersen, 1958)

Stage	Jet Diameter (mm)	Particle Size Range (Microns)
1	1.18	7.0 and above
2	0.91	4.7 – 7.0
3	0.71	3.3 – 4.7
4	0.53	2.1 – 3.3
5	0.34	1.1 – 2.1
6	0.25	0.65 – 1.1

Table 2-2: Particle Size Ranges for Tisch TE-10-800 Viable Cascade Impactor

pressurized meter-dose inhalers. Information from an impactor is then used to determine the active ingredient's particle size, and from the particle size, the likely deposition location of the active therapeutic agent within the respiratory tract (Mitchell, *et al.*, 2003; Stein, 1999).

2.7 Aerospace Corrosion Control

The metal surface of an aircraft, a missile, and associated equipment may become exposed and oxidized during routing use. During scheduled maintenance, workers repair corrosion, beginning with removing the existing coatings. Workers apply coatings over existing coatings in what is called "scuff sand and overcoat." This process removes oxidized paint, and feathers areas where the paint is scratched or chipped. Scuff sanding prepares the surface for coating reapplication (Carlton, 2003b). The most important factor in scuff sanding is to remove the coatings without damaging surfaces.

Prior to application of coatings, the surface must be properly prepared. Hand-held, random orbital sanders mechanically abrade surfaces. Abrasive discs come in various grades or grits. The grit size is related to the particle size on the disc; with smaller numbers corresponding to coarser grits. Scuff sanding usually is done with either 180 or 240 grit (Carlton, 2003b). The sanding generates a wide range of particle sizes, including those less than 10 um. Particles less than 10 um are considered respirable (DiNardi, 1998).

Several studies (Carlton, 2003a, 2003b; Carlton, *et al.*, 2003) document worker exposures during USAF aircraft sanding operations. The ACGIH TLV for SrCrO₄ is 0.5 ug/m³ (ACGIH). The mean reported concentration was 3.93 ug/m³ (95% CI is 2.85-6.42 ug/m³). In a separate study, Carlton (Carlton, 2003a) reports SrCrO₄ TWA exposures

averaged 5.33 ug/m³ (95% CI is 3.4 - 12 ug/m³) during aircraft sanding. These results illustrate that compliance with the new OSHA permissible exposure limit will be difficult.

3 Methodology

In order to investigate Cr dissociation from sanded paint particles in human lung fluid, a method consisting of four distinct phases was used:

- Generate sanding particles from chromate coated aluminum and collect particles in Porcine-SLF
- 2. Quantify the fraction of Total Cr⁺⁶ collected in the Porcine-SLF
- 3. Quantify the Cr⁺⁶ that dissociated from the particles into the Porcine-SLF
- 4. Determine the fraction of Cr⁺⁶ that dissociated

Figure 3-1 visually illustrates all four phases. Particle collection consists of capturing respirable particles generated by sanding aluminum coated with chromate containing primer paints. A viable cascade impactor was used to separate particles within the respiratory range (0.65 microns to 7+ microns) and deposit them into a petri dish containing Porcine-SLF. The Porcine-SLF was created from purified gastric pig mucin that is designed to mimic human lung mucin.

The petri dishes containing Porcine-SLF and sanded particles were incubated for a 24-hour period (the average mucociliary clearance time within the human lung). After incubation, the sample in each petri dish was split into two parts: Dissolved Cr^{+6} and Total Cr^{+6} . The Total Cr^{+6} samples are processed to determine the total amount of Cr^{+6} in the sample regardless of whether the Cr^{+6} is bound in a particle or dissolved. The Dissolved Cr^{+6} samples were processed to determine the amount of Cr^{+6} that dissociated from the particles into the Porcine-SLF. Finally, the amount of Cr in each sample was determined using an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP). The ratio between Dissolved Cr^{+6} and the Total Cr^{+6} is used to calculate the percentage

of Cr⁺⁶ dissociated into the Porcine-SLF.

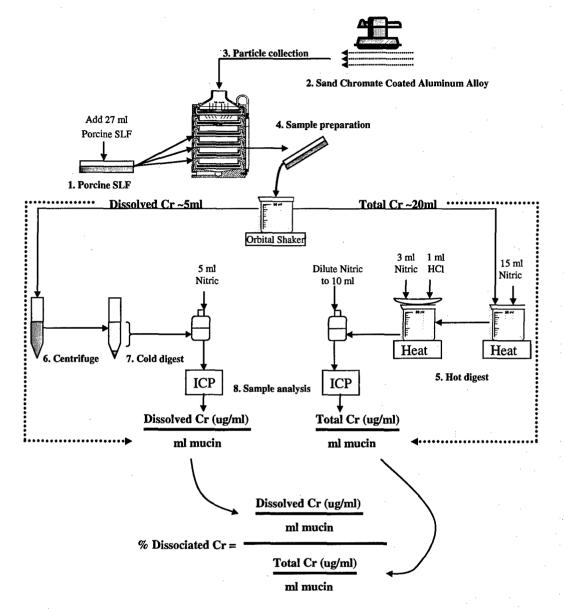


Figure 3-1: Overview of Methodology

3.1 Porcine-SLF (Step 1)

3.1.1 Porcine-SLF Preparation

Materials used to prepare the Porcine-SLF were obtained from Sigma Aldrich (St Louis, MO). The materials were (Sigma Aldrich Product Number): Type II mucin from

porcine stomach (M2378), phosphate buffered saline (P3813), sodium azide (S2002) and dialysis tubing cellulose acetate (D9652).

The Porcine-SLF was prepared based on the method reported by List *et al.* (List, *et al.*, 1978). It was made in 2 to 4-L batches. Isotonic buffer solutions were prepared by adding 0.2 g of sodium azide per 1 L of deionized water in a Pyrex flask. Then, one packet (10 g) of P3813 phosphate buffered saline was added per 1 L. The solution was stirred using a Corning Stirring/Hot Plate Model PC-620 and a 3-inch magnetic Teflon stir bar until all solids were dissolved. The solution had a pH of 7.4. The pH of the solution was lowered by adding concentrated hydrochloric acid (35%) to a pH of 6.6. The pH was measured using an Accumet AR25 pH meter. Next, 40 g of type II mucin was added per 1 L. The resulting solution was stirred at 4°C using a Fisher Thermix Stir Plate and a 2-inch Teflon stir bar for 24 hours.

The resulting Porcine-SLF solution was then purified and low molecular weight (MW) mucin proteins (< 12,000) were eliminated. Proteins with MW greater than 12,000 is consistent with human lung fluid. The Porcine-SLF was purified with centrifugation to remove solids and impurities. Dialysis removed the low MW compounds dissolved in the Porcine-SLF solution.

3.1.2 Centrifugation

The Porcine-SLF solution was poured from the stirring flask into 85 mL Oakridge round bottom centrifuge tubes (approx. 75 mL/tube). The centrifuge rotor held six tubes (approx. 450 mL mucin solution per batch). The solution was centrifuged for 15 minutes at 11,000 rpm and 4 °C. A refrigerated centrifuge was used (Eppendorf 5810 R) with a

fixed angle rotor (F-34-6-38). Following centrifugation, the supernatant was decanted off into 85 mL Oakridge tubes and centrifuged again under the same conditions.

3.1.3 Dialysis

The final supernatant was poured into a 1 L flask. When 1 L of centrifuged Porcine-SLF was collected, it was poured from the flask into dialysis tubing made from cellulose acetate. The tubing was cut into approximately 9-foot lengths. Each 9-foot section of dialysis tubing contained approximately 1 L of centrifuged mucin (110 ml/ft of tubing, per Sigma item description (Sigma-Aldrich, 2005)). The cellulose acetate tubing retains 90% of molecules with MW greater than 12,400 daltons (Sigma-Aldrich, 2005). The dialysis tubing containing the Porcine-SLF solution was placed into an isotonic phosphate buffer solution. The buffer solution, outside the dialysis tubing, was five times the volume of the Porcine-SLF solution, i.e. 1 L of SLF solution was dialyzed in 5 L buffer solution. Small MW molecules were eliminated from the Porcine-SLF by migrating from inside the tube to outside the tube. The Porcine-SLF solution was dialyzed for 24 hours at 4 °C. A covered 5-gallon plastic pail was used for the dialysis. After dialysis, the tubes were removed from the pail and cut; the remaining solution inside the dialysis tube was drained into a flask and allowed to hydrate at 4 °C for 24 hours. The resulting Porcine-SLF solution contained 3 - 3.5% solids by weight and was translucent and slippery to the touch. The Porcine-SLF was stored at 4 °C for short-term storage (2-3 days) and at -79 °C for long-term storage (greater than 3 days).

3.2 Coatings

Four primer paints made by Deft (Irvine, California) that are commonly used by the DoD for corrosion control were used in this study (Table 3-1). These specific primers

	Solvent-Sr	Poly-Sr	Water-Sr	Water-Ba
Deft Product #	02-Y-040A	09-Y-002	44-GN-072	44-GN-007
Military Specs	MIL-P-23377G	TT-P-2760	MIL-PRF-85582D	MIL-PRF-85582C
Base	Solvent based SrCrO ₄	Polyurethane based SrCrO ₄	Water based SrCrO ₄	Water based BaCrO ₄
Properties	Good adhesion, chemical resistant	Low VOC, High flexibility	To reduce VOC emission	To reduce VOC emission
Cr ⁺⁶ by weight in mixed paint	4.78% SrCrO ₄	9.38% SrCrO ₄	5.38% SrCrO ₄ 0.17% BaCrO ₄	2.309% BaCrO ₄ 0.002% ZnCrO ₄

Table 3-1: Primer Paint Specifications

were selected to compare the chromate dissociation of spray painted particles (Moran, 2005) to sanded paint particles. To simulate actual aircraft surfaces, 12" x 12" aluminum alloy 2024 plates were prepared in a manner that included a conversion coating (Henkel Surface Technologies, Madison Heights, MI) followed by the primer coating.

The aluminum used in this study was coated by the Air Force Coatings Technology Integration Office (CTIO). CTIO serves as the Air Force's central resource for aircraft coating system technology and testing. The CTIO maintains a processing line that replicates field surface preparation procedures. This processing line is used to convert, treat, and test aerospace metal panels prior to painting. CTIO assistance was requested to obtain aluminum with coating thickness normally applied to aircraft. CTIO provided 35 aluminum plates for each primer paint. They also provided 20 aluminum plates treated only with the conversion coating.

Prior to sanding the primer paints, 12 blank samples were collected. The 'blanks' consisted of the aluminum plates treated with only the conversion coating. This step was necessary to determine the contribution of Cr⁺⁶ due to the conversion coating when the primer paints were analyzed. These 12 blank samples were handled in the same manner as the primer paints in this study. The results of these blank samples were below the

detection limit of the ICP (0.026 ug Cr /ml mucin), indicating the Cr⁺⁶ contributions from the conversion coating is minimal. Appendix **A-D** contains Material Safety Data Sheets (MSDS) for each paint used.

3.3 Sanding (Step 2)

A Georges-Renault pneumatic random orbital sander (SXRB50) was used to sand the aluminum plates. To control exposure to Cr⁺⁶ during sanding, most sanders are equipped with a vacuum system. The vacuum system is considered an effective engineering control, and is partly the reason that sanding is subject to the new 5 ug/m³ standard. The sander used in this study was not equipped with a vacuum system. The objective of this study was to capture and evaluate respirable particles, which would not have been effective with a vacuum sander. The sander was attached to a compressor with a line pressure of 85 psi. Air pressure at the sander was approximately 78 psi. Sander revolutions per minute (RPM) was estimated with an Extech Combination Contact / Photo Digital Tachometer Model 461895. Photo measurements with a reflective strip were used, since the random orbital revolutions did not allow contact measurement. The estimated orbital speed ranged from 7250 to 7470 RPM. Maximum RPM for scuff sanding is 10,000 (USAF, 2001).

The sandpaper used was 5 inch 3M (St. Paul, MN) Stikit 180-grit Silicon Carbide discs. The discs were self adhesive, attaching to a vinyl disc pad. USAF technical orders specify 120 to 240-grit sandpaper for aircraft scuff sanding. Smaller grit numbers correspond to coarser sandpaper. 180-grit was selected in this study as it is in the middle of this range. Sanding operations lasted until the aluminum under the primer became visible. This reduced the amount of aluminum collected, and is consistent with aircraft

scuff sanding maintenance guidelines (USAF, 2001). Sanding usually lasted 5-10 minutes per aluminum plate (10-15 minutes for Poly-Sr coating). Five aluminum plates were sanded for each sample run. Three cascade impactors collecting simultaneously collected particles during each run. One sanding disc was used per aluminum plate.

A small wooden table (2 ft long by 16 inches wide by 16 inches high) was constructed to conduct the sanding. The height of the table was set so that when the aluminum was placed on the table it would be close to the height of the inlet of the impactor. Ideally, this provided near horizontal particle flow, increasing collection efficiency of the impactors.

Upon completion of a sample run, the tubing was disconnected from the cascade impactors. The cascade impactors were disassembled and petri dishes were gently removed. Care was taken not to disturb the contents of the petri dishes.

3.4 Particle Collection (Step 3)

3.4.1 Paint Booth

A Global Finishing Solutions (FPX-3-BT) portable paint booth was used to draw sanded particles from the sanding operation (Figure 3-2) to three cascade impactors. The working area of the paint booth was 36 inches wide, 35 inches tall and 22 inches deep.

Due to the high airflow, and the shallow depth of the booth, a cardboard extension was placed at the front of the booth to slow particle trajectory from the sander and increase particle capture in the cascade impactor.

3.4.2 Cascade Impactors

Each cascade impactor was assembled with six petri dishes containing 27 ml of Porcine-SLF. The impactors were placed on the inside floor of the paint booth and

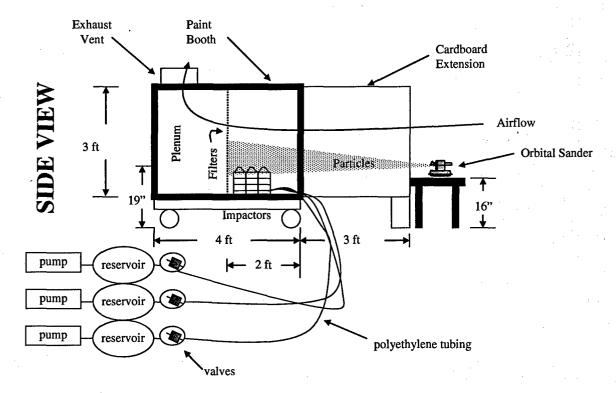


Figure 3-2: Particle Collection Schematic

positioned on the right most side of the paint booth. Preliminary work sanding various materials showed that the impactors collected more particles when positioned in this location. The impactors were assembled in the booth to prevent spilling Porcine-SLF in transport.

3.4.3 Particle Collection System

A sampling train illustrated in Figure 3-2 was set up to capture the particulates from the sanding operation. The three cascade impactors were placed in the paint booth. Each impactor was connected to a rotometer valve, then a reservoir, and then a vacuum pump using polyethylene tubing. The vacuum pumps were GAST 23 series Lubricated Laboratory Vacuum Pump and Compressor. The 4.6 gal reservoir tank was placed between the pump and impactor to reduce airflow oscillations from the vacuum pump. The valve between the impactor and reservoir was used to adjust the airflow rate through

the impactor to 28.3 L/min (1 CFM). The airflow through the collection system was calibrated using a BIOS (Butler, NJ) Drycal DC-2 high flow calibrator, and DC-HC-1 flow cell. The Drycal DC-2 was connected between the valve and the cascade impactor. The pumps were on for at least five minutes to ensure a constant flow through the sampling train. The Drycal DC-2 was turned on and the valves were adjusted until 28.3 L/min was flowing through each impactor. The flow rate was calibrated before each sampling run, and checked after each run to ensure the airflow remained at 28.3 (± 10%) L/min.

3.5 Sample Preparation (Step 4)

After particle collection, the petri dishes were incubated at 37 °C for 24 hours to allow the Cr⁺⁶ to dissociate. Covers were placed on the petri dishes to prevent contamination and evaporation during incubation. After 24 hours, the petri dishes were removed from the incubator. Each petri dish containing Porcine-SLF and sanded particles was transferred to a 50 mL glass beaker. The beakers were weighed before and after adding the sample to obtain the mass of the initial sample collected. Each beaker was then placed on an orbital shaker for 15 minutes at 100 rpm to evenly mix the collected particles in the Porcine-SLF. The samples were then split into two parts: Total Cr⁺⁶ and Dissolved Cr⁺⁶ (as illustrated in Figure 3-1).

3.6 Total Chromate-Hot Digest (Step 5)

The Total Cr⁺⁶ samples contain sanded paint particles that must be digested prior to analysis. The Total Cr⁺⁶ samples were digested in accordance with EPA Method 3010A, which is a digestion method for the preparation of aqueous samples that contain

suspended solids for analysis by ICP (EPA, 1992). Approximately 20 ml of the sample was digested using EPA Method 3010A to determine the total mass of Cr⁺⁶ in the initial samples.

Digestion (Figure 3-1, step 7) began by adding 15 mL of 70% nitric acid to 20 ml of sample in a 50 ml beaker. Each sample was placed on a 95 °C hot plate, and slowly evaporated to a volume of 3-5 mL. The liquid was not allowed to completely evaporate. The beakers were removed from the hot plate and allowed to cool. Then 3 mL of 70% nitric acid was added to each sample and the samples were placed back on the hot plate. The temperature of the hot plate was increased slightly to 105 °C. A watch glass was placed on each beaker and the samples were refluxed. Reflux continued until samples appeared as a lightly colored digestate or there was no change in appearance after continued reflux. At this point, the watch glasses were removed and the sample volume was brought back down to 3-5 ml. The samples were removed from the hot plate and allowed to cool. Finally, 1 mL of 35% hydrochloric acid was added to each sample and the samples were returned to the hot plate with the watch glasses placed back on the beakers. The hydrochloric acid dissolved any precipitates or residue resulting from sample volume reduction. Samples were refluxed for 15 more minutes and then removed from the hot plate and allowed to cool. Before being transferred, the beaker walls were rinsed with 3 mL of 2% nitric acid to minimize losses transferring the samples from the beaker to a centrifuge tube. The samples were then poured into 15 mL Blue Max Jr. polypropylene conical centrifuge tube. A 2% nitric acid solution was added to bring the final sample volume up to 10 mL. These samples were then centrifuged for 20 minutes at 4000 rpm, and 4 °C to remove any remaining non-digestible particles. The supernatant

from the centrifuged samples were then transferred to pre-weighed 30 mL HDPE narrow-mouth sample bottles. The samples and bottles were weighed to obtain the mass of the Total Cr⁺⁶ samples analyzed by ICP. (EPA, 1992; Moran, 2005).

3.7 Dissolved Chromate-Cold Digest (Steps 6-7)

To determine the mass of Cr⁺⁶ that dissociated from the particles into the Porcine-SLF (step 5, Figure 3-1), 5 mL of the initial sample was pipetted into a 15 mL Blue Max Jr. polypropylene conical centrifuge tube. The sample was centrifuged for 20 minutes at 4000 rpm and 4 °C (Kauth, 2001) to remove the solid particulates, leaving only dissociated Cr⁺⁶ in the Porcine-SLF. The supernatant from the centrifuged sample was then poured into a pre-weighed 30 mL HDPE narrow-mouth sample bottle. The bottle was weighed before and after to determine the sample mass. (Moran, 2005)

After the supernatant was transferred to the bottle, 5 mL of 70% nitric acid was added to the 5 mL of centrifuged sample (step 6 of Figure 3-1). The addition of the nitric acid served to digest proteins in the sample prior to analysis and to keep Cr⁺⁶ soluble for ICP analysis. The sample bottle was weighed again after adding acid to calculate the mass that would be analyzed by the ICP for dissolved Cr⁺⁶ concentration. ICP analysis requires metals to be dissolved in a solution. Because this sample already had Cr⁺⁶ in solution and no particles to digest, more aggressive hot digestion was found to be unnecessary. (Moran, 2005)

3.8 Sample Analysis (Step 8)

Samples were analyzed for Cr, strontium (Sr), and barium (Ba). The samples were analyzed for Ba and Sr for quality control purposes. In one molecule of SrCrO₄ and

BaCrO₄, there is one atom of Sr (or Ba) per Cr atom. The sample concentration should be a 1:1 ratio of their respective MWs. The concentration of Cr, Sr, and Ba in each sample was quantified using a Varian Vista-MPX ICP (Figure 3-1, step 8).

Samples were transferred from the 30 mL storage bottles to 15 mL polyethylene test tubes or 20 ml glass test tube, and loaded into the Varian SPS3 auto sampler. For each impactor, the smallest particle size range was analyzed first and the largest particle size range was analyzed last. Blank samples were placed in the auto sampler for each set of 6 samples (the number of petri dishes in each impactor). Blank samples matched the sample matrix; a mixture of 5 mL of Porcine-SLF and 5 mL of 70% nitric acid for Dissolved Cr⁺⁶ and 2% nitric acid for Total Cr⁺⁶. The blanks were to test for carry over between samples.

ICP sample results were reported as micrograms of metal per ml of solute. The mass of each metal (Ba, Cr, and Sr) present in the Dissolved Cr⁺⁶ and Total Cr⁺⁶ samples was calculated by multiplying the ICP result by the volume of the sample in the test tube. The volume of sample in each tube was calculated using the sample mass and a density. The density of the Total Cr⁺⁶ samples was assumed to be 1 g/ml, with a majority of the sample being deionized water with only 2% nitric acid. The density of the Dissolved Cr⁺⁶ was experimentally determined to be 1.1097 g/ml, which equaled the calculated density of a 1:1 ratio of Porcine-SLF and 70% nitric acid.

The mass of metal in each Dissolved Cr⁺⁶ sample and Total Cr⁺⁶ sample was divided by its initial mucin volume, resulting in a mass of Cr⁺⁶ per volume of mucin. The fraction dissociated was determined by dividing the Dissolved Cr⁺⁶ by Total Cr⁺⁶. Figure

3-3 illustrates the calculation of percent dissociation. For specific sample mass calculations see **Appendix E.**

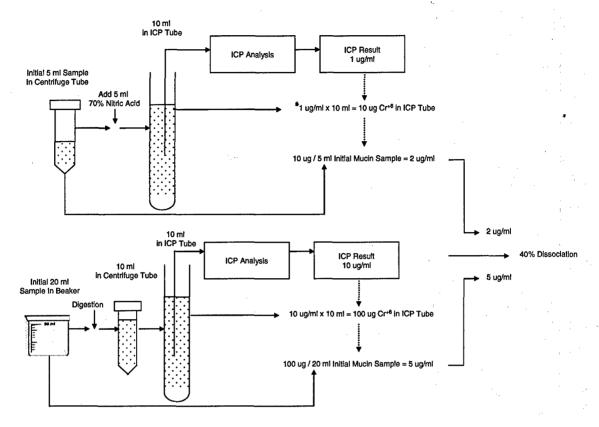


Figure 3-3: Example Calculation Flow Diagram

3.8.1 Inductively Coupled Plasma (ICP) Device

Metal concentrations were determined using the optical emission of excited atoms. Samples travel from the auto sampler, through a nebulizer, spray chamber, and then through a plasma torch. The plasma was created by a radio frequency (RF) coil exciting a stream of argon. The plasma ionizes and excites most metal atoms. Each metal's excited atoms will release light energy in specific wavelengths. The ICP measures the intensity of these specific wavelengths to identify the metal and its concentration. The ICP can detect up to 70 metals simultaneously, and it has five orders of magnitude of linearity that allows for a wide range of concentrations to be analyzed. (Settle, 1997)

The Porcine-SLF had 3-5 % dissolved solids, which was expected in the samples. A "V-groove" nebulizer was selected to analyze these samples. The "V-groove" can handle greater amounts of dissolved solids without clogging. The sample falls under gravity across a high-pressure argon jet. The argon jet shears the sample into small droplets. The nebulizer is inserted into the spray chamber. In the spray chamber, the larger droplets fall out, and only a fine mist is allowed up into the plasma torch. (Moran, 2005)

ICP can use two plasma viewing configurations: radial view and axial view. The axial view is parallel to the argon flow while the radial view is perpendicular to the argon flow. The radial view utilizes in-line venting, which reduces blockages due to solids. The radial view has become the industry standard for high dissolved solids applications. A radial torch configuration was used in this study due to the expected solids. (Varian, 2001) The ICP was operated using the settings provided in Table 3-2.

Condition	Setting	Condition	Setting
Power	1.2 kW	Replicate Read Time	10 sec
Plasma Flow	15.0 L/min	Instrument Stabilization Delay	15 sec
Auxiliary Flow	1.5 L/min	Sample Uptake Delay	25 sec
Nebulizer Pressure	190 kPa	Pump Rate	15 rpm
Viewing Height	10 mm	Rinse Time	75 sec
Replicates	3		

Table 3-2: Vista-MPX ICP Settings

3.8.2 Calibration Standards

Six standard solutions (50 ppb, 200 ppb, 500 ppb, 1 ppm, 10 ppm, 50 ppm) were prepared from a 50 ppm Varian Tuning Solution for Total Cr⁺⁶ analysis. Five standard solutions (50 ppb, 200 ppb, 500 ppb, 1 ppm, 10 ppm) were prepared from the Varian Tuning Solution for Dissolved Cr⁺⁶. Previous experiments showed Dissolved Cr⁺⁶ concentrations were less than 10 ppm, therefore the 50 ppm calibration standard was not

used in Dissolved Cr⁺⁶ analysis. Standards were prepared in a matrix that closely matched the sample matrix that was introduced into the ICP. For Total Cr⁺⁶ samples, which consisted of digested metals in a dilute nitric acid solution, the calibration standards were prepared in 2% nitric acid. For Dissolved Cr⁺⁶ the standard matrix was also a 50/50 mixture of Porcine-SLF and 70% nitric acid. These calibration standards were spiked with the appropriate amount of known standard to achieve the desired concentration. The software was set to fail if the R² of the calibration curve was less than 0.995. A blank sample was added following each calibration. Then, a check sample of 500 ppb was used with the Dissolved Cr⁺⁶, and 1 ppm for the Total Cr⁺⁶. The software was set to discontinue sampling if the check samples were +/- 10% of the expected measurement.

3.8.3 Internal Standard

A 2-ppm rhodium solution (in 2% nitric acid) was used as an internal standard. The ICP automatically incorporated the internal standard into the sample stream with its peristaltic pump and "Y" connector. This ensured that each sample was spiked with the same amount of internal standard.

3.9 Solubility in SLF

The Water Solubility test (OECD, 1987) was used as the basis to determine the solubility of SrCrO₄ in Porcine-SLF. Cascade impactors were set up in the same manner as the data collection of sanded particles. The pumps were calibrated to an airflow of 28.3 L/min. A small box (8.5" x 8.5" x 13") was constructed with a ¼" diameter hole in the end, three 1" diameter round holes in the side and three 1" diameter round holes (diameter of cascade impactor inlet) on the bottom. Figure 3-4 provides a visual concept

of this set up. This box was placed on top of the impactors, with only the impactor inlet inside the box. A small amount of SrCrO₄ powder was placed in a small dish, and the dish was placed in the box. The box was then closed. A pneumatic blow gun tip was inserted into the ½" hole, and was used to aerosolize the powder inside the box.

Air Enters Through 1" Holes Raw SrCrO₄ Powder Air Gun Aerosolizes SrCrO₄ Impactors

Figure 3-4: Raw SrCrO₄ Collection Schematic

After five minutes, the box was removed from the tops of the impactors and the pumps were disconnected from the impactors. Twelve impactors of 6 petri dishes each (72 samples) were taken. Nine sets of petri dishes were allowed to incubate for 24 hours at 37 °C. These samples were for direct comparison to the samples of sanded particles in Porcine-SLF.

Airflow

Three sets of petri dished were allowed to incubate for 72 hours at 45° C, and then for 24 hours at 37° C. This modification was used to determine the solubility of raw strontium chromate in Porcine-SLF. Guidelines from *Water Solubility* recommend

dissolving particles above the test temperature, and when solubility has been achieved reduce the temperature back to the test temperature. Using this method, solubility was determined to be 86 ug/ml. Dissolved Cr⁺⁶ samples in this study were less than 22 ug/ml, and dissolved raw SrCrO₄ samples were less than 35 ug/ml. The Cr⁺⁶ from sanded particles will not completely dissociate if the concentration sampled saturates the Porcine-SLF. This test verified that the upper limit had not been reached, and saturation was not the limiting factor in dissociation results.

3.10 Detection Limits

The Cr⁺⁶ from sanded particles may not be accurately measured if the concentration is at or below the instrument's detection limit. The detection limit was determined following procedures in 40 CFR Part 136, Appendix B "Definition and Procedures for the Determination of the Method Detection Limit". The detection limits were determined for Ba, Cr and Sr in 1:1 Porcine-SLF:nitric acid (Dissolved Cr⁺⁶ samples) and 2% nitric acid (Total Cr⁺⁶ samples). Twelve replicates for each matrix were analyzed. Three times the average standard deviation was used to calculate the detection limit for each metal. Table 3-3 lists the results.

	Barium (ug/ml)	Cr (ug/ml)	Sr (ug/ml)
Porcine-SLF	2	11	3
Wavelength	455.403 nm	283.563 nm.	407.771 nm
2% Nitric	1	10	1
Wavelength	455.403 nm	267.716 nm	407.771 nm

Table 3-3: ICP Detection Limits

4 Results

4.1 Sanded Paint Particle Dissociation

Figure 4-1 is a summary of the results from the four types of paint and raw SrCrO₄ with 95% confidence intervals. Dissociation of Cr⁺⁶ was plotted for each of the six particle size ranges. Summaries of dissociation for each paint type are available in **Appendix F**.

Hexavalent Chromium Dissociation

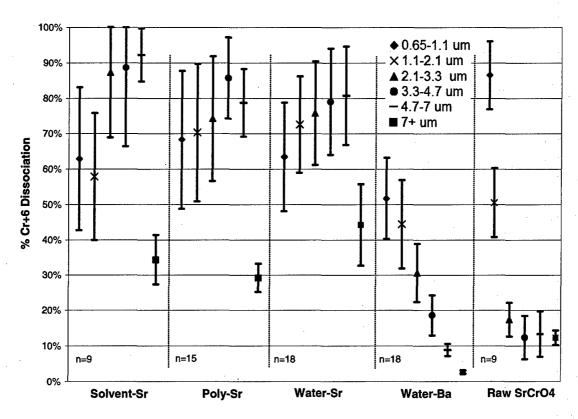


Figure 4-1: Percent Cr⁺⁶ Dissociation from Sanded Particles into Lung Fluid by Particle Size

Note: Symbol is mean and bars represent the 95% Confidence Intervals

4.1.1 General Trends

Figure 4-1 reveals the mean percentage of Cr⁺⁶ dissociation into Porcine-SLF was relatively high for the three SrCrO₄ paint types, with means ranging from 58-92%. The

BaCrO₄ paint dissociated less Cr⁺⁶ than SrCrO₄, with means ranging from 9-52%.

Interestingly, the raw SrCrO₄ dissociated less Cr⁺⁶ than all the paint types in the largest four particle sizes ranging from 12-20%.

The Cr⁺⁶ dissociation of raw SrCrO₄ is comparable to the sanded particles of the SrCrO₄ paints in the smallest two particle size ranges. The 0.65-1.1 um particles dissociated 86%, followed by 50% in the 1.1-2.1 um size particles. The largest 4 particle size ranges dissociated significantly less Cr⁺⁶ than the sanded SrCrO₄ particles.

4.1.2 Raw SrCrO₄

The raw SrCrO₄ was collected in slightly higher concentrations than the sanded paint particles, but all concentrations were below saturation and above the lower detection limit. The raw SrCrO₄ particles were completely immersed and appeared near the bottom of the petri dish, whereas most sanded particles remained immersed but suspended in the Porcine-SLF near the surface.

The physical characteristics of a sanded particle compared to a raw SrCrO₄ particle may explain why the raw SrCrO₄ released less Cr⁺⁶. Raw SrCrO₄ and sanded particles were viewed under a microscope. Figure 4-2 is a microscopic example of 7+ um sized raw SrCrO₄. Figure 4-3 is a microscopic example of 7+ um sized Solvent-Sr sanded paint particles. Larger rod shaped particles are clearly visible in the raw SrCrO₄ particles, while the sanded particles are much smaller. Sanded particles are created by shearing the painted surface, which creates smaller, non-spherical particle size. These smaller sanded particles have a larger exposed surface area to the Porcine-SLF, and therefore should dissociate more Cr⁺⁶ than the larger raw SrCrO₄ particles.

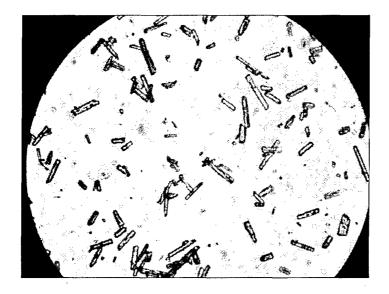


Figure 4-2: Raw SrCrO₄, 100x Magnification, 7+ um Particle Size

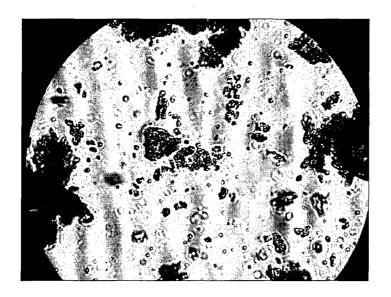


Figure 4-3: Solvent-Sr Sanded Paint Particles, 100x Magnification, 7+ um Particle Size

Another explanation could be that the raw SrCrO₄ may have become saturated in areas of close proximity to the particles. Since the petri dishes were at rest for 24 hours, there was no mixing. The Porcine-SLF is a viscous substance and with no mixing, the dissolved SrCrO₄ could not evenly distribute throughout the Porcine-SLF. If this phenomenon had occurred with the sanded particles, the impact would not be as

influential because the larger surface area from smaller, non-uniform particles would saturate a larger fraction of the Porcine-SLF.

4.1.3 Particle Size Comparison Within Paints

Slight differences in dissociation are seen when looking at the particle sizes within each of the paints. There are no statistical differences in the SrCrO₄ paints, although there is a slight trend of less dissociation in the smaller particles. The trend is reversed in BaCrO₄, with the smallest particles sizes dissociating more Cr⁺⁶ than the larger particles. Particle size appears to have some influence on the dissociation of Cr⁺⁶ from sanded paint particles.

Each paint exhibited a sharp drop in dissociation of particle sizes greater than 7 um. This may be explained by visual observations of the petri dishes before and after incubation. Prior to incubation, the upper two particle size ranges (4.7-7 um and 7+ um) appeared to have particles floating on the top of the Porcine-SLF. After incubation, the particles in range 4.7-7 um appeared to become fully immersed in the Porcine-SLF. Particles greater than 7 um did not appear to fully immerse in the Porcine-SLF even after incubation. If the Cr⁺⁶ were not in contact with the Porcine-SLF, Cr⁺⁶ would not be able to dissolve into the Porcine-SLF. This was verified by observing the petri dishes under a microscope. All other particle size ranges were completely immersed in the Porcine-SLF prior to incubation. Therefore, the 7+ um particles may have a low Cr⁺⁶ dissociation because they were not in full contact with the Porcine-SLF.

4.2 Sanded Particle - Paint Particle Comparison

Figure 4-4 illustrates the side by side comparison of sanded and painted particles for each paint type. A previous study (Moran, 2005) investigated the dissociation of freshly

sprayed primer paint particles in Porcine-SLF. The results of that study showed that smaller SrCrO₄ particles (<2.1 um) dissociated less Cr⁺⁶ than larger particles (>2.1 um), which matches a general trend observed with the sanded particles. It also showed that Water-Ba dissociated significantly less Cr⁺⁶ than all SrCrO₄ primers. A comparison of the dissociation of sanded particles was made to the results of the spray paint dissociation.

The 7+ um particle sizes are shown in Figure 4-4, but are not included in the analysis because they were not fully immersed like all the other particles. With the exception of the largest particle size range (7+ um), Poly-Sr and Water-Ba sanded particles dissociate significantly more Cr⁺⁶ than the same paint particles. For Solvent-Sr and Water-Sr, the sanded and freshly sprayed paint particles appear to behave in a similar manner.

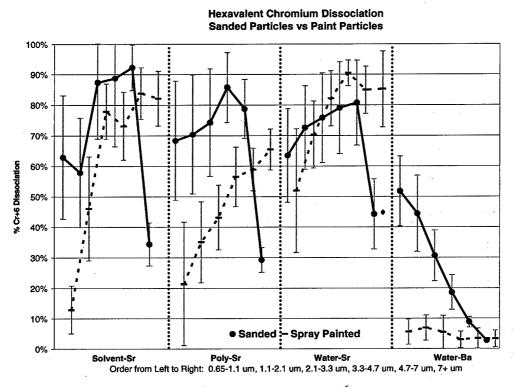


Figure 4-4: Comparison of Sanded vs Paint Particle % Cr⁺⁶ Dissociation

Note: Symbol is the Mean and bars represent the 95% Confidence Intervals

4.3 Particle Collection Analysis

Figure 4-5 illustrates the Dissolved Cr⁺⁶ (ug Cr⁺⁶/ml mucin) for all samples. Figure 4-6 illustrates the Total Cr⁺⁶ (ug Cr⁺⁶/ml mucin) collected for all samples. The percent dissociated results illustrated in Figure 4-1 were determined by dividing the Dissolved Cr⁺⁶ by the Total Cr⁺⁶ in Figures 4-5 and 4-6. Three sample concentrations for Solvent-Sr and two concentrations for Poly-Sr were calculated to be at the detection limit.

4.4 Statistical Analysis

Statistical analysis was performed using SPSS version 12.0 (SPSS Inc., Chicago, II) statistical software package. Analysis of variance (ANOVA) tests were used to evaluate the data. ANOVA was used to determine if there were differences between particle size and paint type. The assumptions made in this determination are that the sample

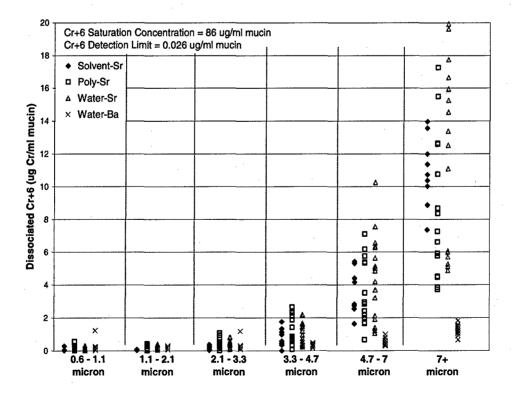


Figure 4-5: Sanded Paint Particle Cr⁺⁶ Dissociation into Lung Fluid by Particle Size

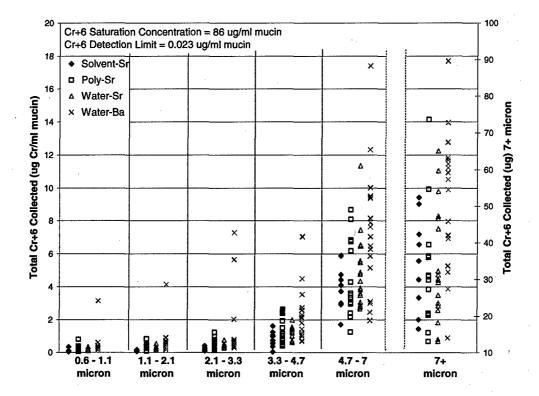


Figure 4-6: Sanded Paint Particle Total Cr⁺⁶ Collected by Particle Size populations were random and independent of each other. Also, the sample populations were assumed to have a normal distribution and equal variance.

4.4.1 Normality

To test the normality of the sample populations, Quantile-Quantile (QQ) plots were created for each paint type and raw SrCrO₄. These plots compare the observed percentile of sample data to the expected percentile of a standard normal distribution. Normal data lies on a 45-degree line. Figure 4-7 displays an example QQ plot for the Solvent-Sr primer. The plotted data for all paints did not significantly deviate from the 45-degree line; so the assumption of normality was assumed to be valid. **Appendix H** contains QQ plots for the remaining paints and raw SrCrO₄.

4.4.2 Analysis of Variance (ANOVA)

Initially, a two way ANOVA test was run to determine if there was interaction between the two variables of interest: particle size and paint type. The test showed significant interaction (p<0.001). One-way ANOVA tests were used to compare the means within each of the different paints, and the means of particle sizes among the different paints.

Normal Q-Q Plot of Percent Dissociation

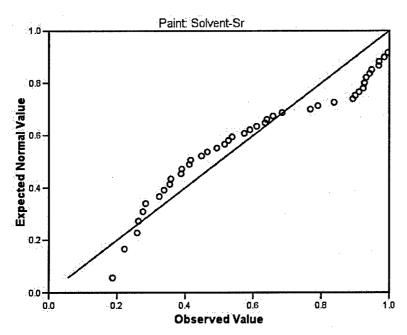


Figure 4-7: Normal Q-Q Plot for Dissociation of Sanded Solvent-Sr Primer Particles

4.4.3 Particle Size Comparison

Comparison of Cr^{+6} dissociation between the six particle-size ranges within each paint was made using one-way ANOVA. The ANOVA comparisons were performed at an overall significance level of $\alpha = 0.05$. Examination of each paint revealed statistical differences in Cr^{+6} dissociation between particle sizes within the paint (Solvent-Sr (p<0.000), Poly-Sr (p<0.000), Water-Sr (p<0.002), Water-Ba (p<0.000) and the raw

SrCrO₄ (p<0.000). The significant differences for the Poly-Sr and Water-Sr may be due to the issues with particle sizes greater than 7 um as described earlier.

Comparison of the mean dissociation of the particle sizes within each paint are shown in Figure 4-8. In this figure, the means of particle size ranges within the paint are grouped where they are not statistically different (underlined groups). For the three SrCrO₄ paints, the particle size range from 1.1 - 4.7 um shows no statistical difference, although there is a trend where more Cr⁺⁶ appears to dissociate as particle size increases (except 7+ um particles likely because they did not fully immerse). The BaCrO₄ paint and raw SrCrO₄ tend to dissociate less Cr⁺⁶ as particle size increases.

	0.65-1.1 μm	1.1-2.1 μm	2.1-3.3 µm	3.3-4.7 μm	4.7-7 μm	7+ µm
Mean	63%	58%	84%	85%	92%	34%
		Pikesayanadya, Color Indi arangan Tahungan				
Solvent-Sr						
Mean	68%	70%	74%	86%	79%	29%
Poly-Sr						
Mean	63%	72%	76%	79%	81%	44%
Water-Sr						
Water-Sr						
Mean	52%	44%	31%	19%	09%	27%
		Taking Taking Salah Salah				
Water-Ba						
	Land the first of the second s					
Mean	86%	50%	17%	12%	13%	12%
Raw SrCrO ₄						
Raw SICIO						

Figure 4-8: One way ANOVA Particle Size Comparison of %Dissociation Within the Paint Types

(Horizontal bar indicates "no significant difference" between underlined groups)

4.4.4 Paint – Paint Comparison

Comparison of Cr⁺⁶ dissociation between the four paints and raw SrCrO₄ was made using one-way ANOVA. The same particle size in each of the four paints was examined. This examination revealed statistical differences of Cr⁺⁶ dissociation for each of the four paints and the raw SrCrO₄ at each particle size except 1.1 - 2.1 um. The three SrCrO₄ paints did not have any differences except the 7+ um size particles. The significant difference between the four paints was due to the low BaCrO₄ and raw SrCrO₄ dissociation.

Comparison of the means of the paints at each particle size are shown in Figure 4-9. In this figure, the means are grouped where they are not statistically different (underlined groups). For the three SrCrO₄ paints, the means at each particle size are not significantly different (except 7+ um particles likely because they did not fully immerse). The BaCrO₄ paint and raw SrCrO₄ were significantly different from the SrCrO₄ paints in the smallest two particle size ranges.

4.5 Quality Control

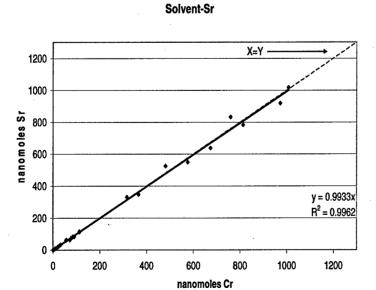
The standard method used in this research measured Cr, Sr, and Ba in each sample. The total moles of Sr or Ba (per ml of mucin sample) were plotted against the total moles of Cr for the paints. The line of 'best fit' was drawn, assuming the line passes through the origin. The equation of the line, as well as the line's R² was added to the graph. For reference, a dashed line labeled 'X=Y' was added to the graphs, which symbolizes perfect 1:1 molar ratios. Figures 4-10 to 4-14 contain these graphs. Solvent-Sr, Water-Sr, Water-Ba, and raw SrCrO₄ were found to have approximately the expected 1:1 ratio

	Solvent-Sr	Poly-Sr	Water-Sr	Water-Ba	Raw SrCrO4
Mean	34%	29%	44%	3%	12%
	Table 1 Table 1 Section 1	<u>la de la capación de la esta esta esta esta esta esta esta est</u>			
7+ µm					
Mean	92%	79%	81%	9%	13%
Wican					
4.7-7 µm					
Mean	85%	86%	79%	19%	12%
	en en en 1905 en en 1905 en en 1905 en En 1905 en 190				
3.3-4.7 µm					
Mean	84%	74%	76%	31%	17%
		n unggaberse			
2.1-3.3 µm					
Mean	54%	70%	72%	44%	50%
1.1-2.1 µm	The state of the s				
1.1-2.1 μm					
Mean	65%	68%	65%	52%	86%
	<u>amang ng kelala</u>	e e no ser transcer, significa		ugraja iki a kunggia déngasa, ég	
0.65-1.1 µm					
No bridge 250	ugaby, i, Fridg				

Figure 4-9: One way ANOVA Paint Type Comparison of %Dissociation among Particle Sizes

(Horizontal bar indicates "no significant difference" between underlined groups)

of Cr to Sr (or Ba). The Poly-Sr paint appeared to deviate about 20 percent, largely influenced by a few data points, with an R² of 0.95.



Total Cr vs Total Sr

Figure 4-10: Solvent-Sr Cr:Sr Ratio

Total Cr vs Total Sr Poly-Sr

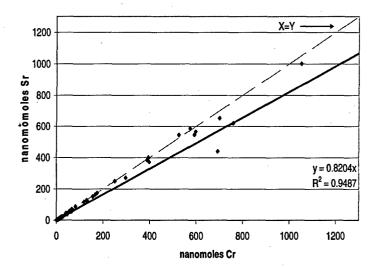


Figure 4-11: Poly-Sr Cr:Sr Ratio

Total Cr vs Total Sr Water-Sr

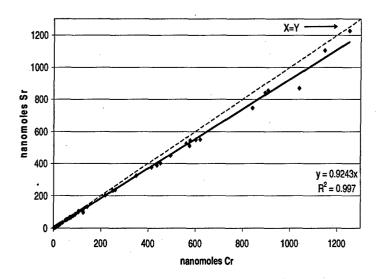


Figure 4-12: Water-Sr Cr:Sr Ratio

Total Cr vs Total Ba Water-Ba

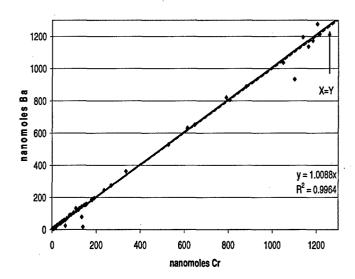


Figure 4-13: Water-Ba Cr:Ba Ratio

Total Cr vs Total Sr Raw SrCrO4

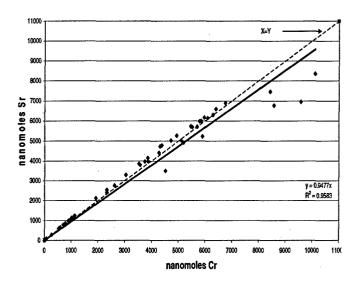


Figure 4-14: Raw SrCrO₄ Cr:Sr Ratio

5 Discussion

5.1 Chromate Dissociation

The results of this research show that SrCrO₄ based sanded particles releases most of their Cr⁺⁶. Another observation is SrCrO₄ based sanded particles release more Cr⁺⁶ than BaCrO₄ particles. When comparing sanded particles to raw SrCrO₄ particles, sanded particles release significantly more Cr⁺⁶. When comparing sanded particles to paint particles, sanded particles release significantly more Cr⁺⁶ in Poly-Sr and Water-Ba paints, while there was no difference in the Solvent-Sr and Water-Sr paints. Studies have implied there is a protective mechanism in paint particles resulting in painters not having an increased lung cancer risk. The implication of this study showing sanded particles releasing more Cr⁺⁶ is that there is no protective mechanism, confirming theories that sanders may have increased lung cancer risk.

There is a slight trend that suggests both smaller SrCrO₄ paint and sanded particles release a smaller percentage of Cr⁺⁶ than larger particles. Statistical differences between particle sizes within the SrCrO₄ paints were not consistent, although there was a significant drop in the largest particle size range. This is believed to be due to particles clumping and mounding at the surface of that petri dish and not being immersed into the Porcine-SLF. The overall dissociation of BaCrO₄ primer is significantly less than the SrCrO₄ for both paint and sanded samples.

The paint matrix significantly affected Cr⁺⁶ dissociation. The SrCrO₄ paints had

significantly more Cr⁺⁶ dissociation compared to the BaCrO₄ paints, for both sanded and freshly sprayed paint particles. **Appendix G** contains a summary of means and standard deviations for each sanded paint type.

The raw SrCrO₄ sampled as a control displayed opposite trends as the sanded paint samples. The mean Cr⁺⁶ dissociation was statistically the same as the SrCrO₄ paints for the smallest particle size range and statistically the same for all paints for the 1.1-2.1 um particle sizes. Dissociation of Cr⁺⁶ from the four largest raw SrCrO₄ particle size ranges subsequently dropped to 12-20%. This suggests that time possibly plays a role in dissociation of larger particles. 24 hours may not be enough time for full dissociation of raw SrCrO₄. Another possibility to explain the sudden drop in dissociation is localized saturation. Porcine-SLF is a thick, viscous liquid. It is possible that areas immediately surrounding large particles reach saturation for Cr⁺⁶ and the physical properties of the Porcine-SLF do not allow further dissociation in this localized area.

5.2 Particle - Lung Fluid Interaction in Lungs

Together, the two layers of human lung fluid range from 5-10 um in depth. The watery sol layer depth ranges from 3.6-6 um (average length of cilia). Therefore, the depth of the mucus layer is most likely 1.4-4 um. Observations in this study showed particles 7+ um did not completely submerge. When viewed in terms of the human lung, it is likely that particles would also not completely submerge in the mucous layer of the human lung. Figure 5-1 illustrates this concept. The actual thickness of the mucus layer is only 2-4 um thick. Larger particles therefore would physically be unable to completely immerse in the mucosal layer.

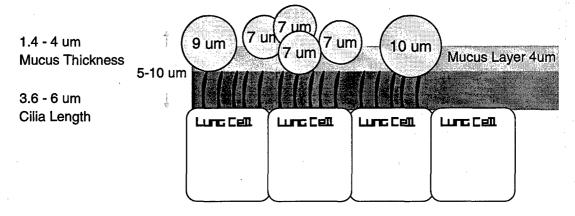


Figure 5-1: 7+ um Particle Interaction with Human Lung Mucus Layer

5.3 Limitations

Several potential biases exist in these results. The ICP provided more consistent results using a 0.050 ug/ml calibration standard versus any lower concentration.

Dissolved Cr⁺⁶ concentrations, especially in the smaller particle size ranges, may have been near or below the instruments detection limits for Cr (0.026 ug/ml). Five sample results that were near the detection limit were changed to the detection limit. Systemic error may have been introduced through splitting the samples for Dissolved Cr⁺⁶ and Total Cr⁺⁶. Prior to splitting, the samples were shaken for 15 minutes. The assumption was made that the samples were a homogenous mixture. When splitting the samples, the Porcine-SLF may not have been entirely homogenous, concentrating the sanded particles in one location. This potentially allowed a disproportionate amount of solid particles to be pipetted from the sample into the dissolved portion. Then, these particles were removed during centrifuging. This would potentially decrease the Total Cr⁺⁶ and thereby increase the percent dissociated.

5.4 Future Work

This study utilized a method to determine what fraction of contaminants entering the lung are available for uptake. The method used in this study effectively captured respirable particulates of a contaminant and deposited them into a petri dish containing Porcine-SLF. This study successfully showed Cr^{+6} dissociating from sanded paint particles into a lung fluid, and quantified the bioavailability of a carcinogenic material. This method can be used to study the bioavailability of chemicals in the lungs due to aerosol or dust inhalation.

To be biologically significant, particles entering the lungs must pass through the mucus layer and the sol layer, before it interacts with lung tissue. The Porcine-SLF used was representative only of the mucus layer. The results of this study indicate that a large fraction of Cr^{+6} dissociates from the sanded paint particles into the Porcine-SLF. Possible follow on studies could determine the fraction of Cr^{+6} in the mucus layer that reaches the lung tissue after passing through the watery sol layer.

In healthy lungs, cilia constantly beat, transporting mucus out of the lungs. This research utilized a simulated mucus solution, but did not account for movement and mixing due to the cilia by incubating petri dishes at rest. The results of the largest particle size range in this study would most likely show additional dissociation if allowed to mix and incorporate the clumped particles into the Porcine-SLF. A slow stir during the incubation step of this would address this limitation.

Large quantities of particles were generated in order to achieve a detectable concentration in the small particle size ranges. The low concentrations dissociated significantly more Cr⁺⁶ than the largest concentrations of particles. A potential effect

may be one of higher concentrations dissociating less than low concentrations regardless of particle size. Similar Total Cr⁺⁶ concentrations in each particle size range would eliminate this effect and allow for a more unbiased comparison between particle sizes. Further, it is not clear why the raw SrCrO₄ dissociation dropped off so quickly considering that the samples were roughly 50% of the solubility limit. Additional studies are needed to determine whether this was due to a time factor, mass factor, or other unknown cause.

Finally, to reduce confounding variables, this study utilized one type of abrasive to generate particles. Initial work prior to data collection indicated that different dissociation effects may be seen using other sizes of abrasive grit. A determination as to whether larger grit causes larger particulates, and if those larger particles dissociate additional Cr⁺⁶ is needed to fully understand the risk to those in the sanding occupations.

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Appendix A. MSDS for Solvent-Sr Paint parts A & B

~~~~	. rot coactings,			evised : 10					
	SECTION		NDENTIFICATION						
Manufacturer:	DEFT, INC. (CAGE 17451 VON KARMAN	CODE 33461) AVENUE	Information Ph Emergency Ph CHEMTREC Ph	one: (949) one: (800) one: 800-42	174-0400 124-9300 1-9300				
	IRVINE 92614	.CX							
Trade Name :	TYPE I, CLASS C MIL-PRF-23377H, 02Y040A NONE	COMPONENT A	1 0> 4	s: Hea me P. Reactiv	th - 4 ire - 3 ity - 1				
	SECTION	II - HAZARDOU	s ingredients						
					Emperire	Limits		-	
Tnarodi onte		me k	Weight	नग <b>ः</b> ।	CGIH	DET	OSHA STEP		VP
angreuzenca									HUN MO
METHYL n-AMYL BENZENE, 1-CHLC STRONTIUM CHRC	KETONE PRO-4 TRIPLUOROMET MATE	110-43-0 HYL 98-56-6 7789-06-2 The	5.740 1.680 19.130 ACGIH TWA for S	50 ppm N.E. 5 trontium Ch	N.E. N.E.	100 ppm N.E. .1 mg/M3 7789-06-2)	N.E. N.E. N.E. as Cr	2.6 5.3	9 68F
TITANIUM DIOXI	DE	13463-67- ACGT	7 2.930 R/TLV & OSHA/PE	10 mg/M3 Exposure	N.E. limits are	15 mg/M3 for total d	N.E.		
AMORPHOUS SILI n-BUTYL ACETAT METHYL n-PROPI	CA PE L KETONE HOL	7631-86-9 123-86-4 107-87-9	0.000 1.230 14.660	10 mg/M3 150 ppm 200 ppm	10 mg/M3 200 ppm 250 ppm	80 mg/M3 150 ppm 200 ppm	80 mg/M3 200 ppm 250 ppm	13 27.8	# 68F
	VE LISTED PRODUCTS				N.E.	add nc	M.E.	B 0	A .00t
	UNLISTED INGREDI		CW THANKILOWA PIT	or.					
N.E. = Not Est	ablished								
	SECTI	ON III - PHYS	ICAL DATA						
Boiling Range: Evap. Rate: Volatiles vol	213 - 306 Deg 1.37 x n-Butyl 8 44.3 Wgt%	. r Vaj Acetate Li 24.1 Wg	por Density: He quid Density: He t per gallon: pec. Gravity:	eavier than 12.68 Pound 1.52221	Mater. Nater. ls.				
V.O.C.: 35 SOLUBILITY IN	WATER: Insoluble EMPERATURE: No in:	SOLVENT ODOR  PH: Not formation found	applicable	5,55					

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MATERIAL SAFETY DATA SHEET Printed: 07/22/04 For Coatings, Resins and Related Materials
Page: 1
IRVINE
Product Class: TYPE I, CLASS C | Hazard Ratings: Health - 3 | none -> extreme | Fire - 3 | rade Name : MIL-PRF-23377H, COMPONENT B | 0 --> 4 | Reactivity - 1 | C.A.S. Number: NONE | Personal Protection - 2
```

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight	TLV	- Exposure CGIH STEL	Limits	SHA STEL	VP mm HG
D-BUTYL ALCOHOL PETROLEUM NAPHTHA LT. AROMATIC 1,2,4 TRIMETHYLBENZENE CUMENE 1,3,5 TRIMETHYLBENZENE AMINO SILANE ESTER	71-36-3 64742-95-6 95-63-6 98-82-8 108-67-8 1760-24-3	9.660 6.640 6.870 0.340 1.890	50 ppm 100 ppm 25 ppm 50 ppm 123 mg/M3 200 ppm	N.E. N.E. 35 ppm N.E. N.E.	50 ppm N.E. N.E. 50 ppm N.E. 200 ppm	N.E. N.E. N.E. N.E. 250ppm	4.4 @ 68F 3 Ø 68F

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST. ALSO ANY UNLISTED INGREDIENTS.

#### N.E. = Not Established

SECTION III - PHYSICAL DATA

SECTION III - PHYSICAL DATA

Boiling Range: 244 - 401 Deg. F Vapor Density: Heavier than Air.
Evap. Rate: 0.36 x n-Butyl Acetate Liquid Density: Lighter than Water.
Volatiles vol % 41.4 Wgt% 38.6 Wgt per gallon: 8.04 Founds.
Spec. Gravity: 0.96519

Appearance: AMBER LIQUID WITH SOLVENT ODOR
V.O.C.: 259 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOIGNITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSION RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 02Y040A
PER INSTRUCTIONS.

# Appendix B. MSDS for Poly-Sr Paint parts A & B

```
MATERIAL SAFETY DATA SHEET
                                                                                       Printed: 07/22/04
  Page: 1
                           For Coatings. Resins and Related Materials
                                     Revised: 12706/01
                      SECTION I - PRODUCT INDENTIFICATION
  Manufacturer: DEFT, INC. (CAGE CODE 33461)
17451 VON KARMAN AVENUE
                                                                    Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300
                                                                   Hazard Ratings: Health - 4 none -> extreme Fire - 3 Reactivity - 1
  Product Class: POLYURETHANE
  Trade Name : TT-P-2760A TYP 1 CLASS C
Product Code : 09Y002
                                                                                Personal Protection - I
  C.A.S. Number: NONE
                                 SECTION 11 - HAZARDOUS INGREDIENTS
                                                                                        ----- Exposure Limits ----
                                                                            Weight
                                                                                                ACGIH OSHA
TLV STEL PEL
  Ingredients
                                                     CAS #
  n-BUTYL ACETATE
ETHYL 3-ETHOXYPROPIONATE
                                                      123-86-4 3.970 150 ppm 200 ppm 150 ppm 200 ppm
763-69-9 10.280 N.E. N.E. N.E. N.E.
                                                    DISPERSION AID
  ISOBUTYL ALCOHOL
  STRONTIUM CHROMATE
  TITANIUM DIOXIDE
  METHYL ETHYL KETONE
2-4 PENTANEDIONE
  DIBUTYLTIN DILAURATE
          THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
 N.E. = Not Established
evap. Rate: 0.66 x n-Butyl Acetate Liquid Density: Heavier than Air. Evap. Rate: 0.66 x n-Butyl Acetate Liquid Density: Heavier than Water. Volatiles vol % 28.4 Wgt % 19.0 Wgt per gallon: 11.53 Pounds. Spec: Gravity: Appearance: BEOWN LIQUID WITH SOLVENT ODOR V.O.C.: 262 G/L SOLUBILITY IN WATER: Insoluble PH: Not applicable AUTOIGNITION TEMPERATURE: No information found DECOMPOSITION TEMPERATURE: No information found CORROSION RATE: No information found VISCOSITY: Thin liquid to heavy viscous material
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MATERIAL SAFETY DATA SHEET
                                                                                               Printed: 07/22/04
 Page: 1
                            For Coatings, Resins and Related Materials
Revised: 12/06/01
                                  SECTION I - PRODUCT INDENTIFICATION
Manufacturer: DEFT, INC. (CAGE CODE 33461)
17451 VON KARMAN AVENUE
                                                                           Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300
                                                                          | Hazard Ratings: Health - 4 | none -> extreme | Fire - 3 | 0 ---> 4 | Reactivity - 1
Product Class: ALIPHATIC ISOCYANATE
Trade Name : CAT,TT-P-2760A,TYP 1,CL C
Product Code : 09Y002CAT
 C.A.S. Number: NONE
                SECTION II - HAZARDOUS INGREDIENTS
                                                                                      Weight ACGIH OSHA
TLV STEL PEL STEL
 Ingredients
                                                           CAS #
                                                                                                                                                                                 mm HG
 POLYMERIC HEXAMETHYLENE DIISOCYANAT 28182-81-2 55.530
                                                                                                   N.E. N.E.
  822-06-0
METHYL ISOBUTYL KETONE

N-BUTYL ACETATE

METHYL ETHYL KETONE

ORGANOSILANE ESTER
          THE ABOVE LISTED INGREDIENTS ARE ON THE TSCA INVENTORY LIST, ALSO
          ANY UNLISTED INGREDIENTS.
N.E. = Not Established
SECTION III - PHYSICAL DATA

Boiling Range: 175 - 460 Deg. F Vapor Density: Heavier than Air.
Evap. Rate: 2.92 x n-Butyl Acetate Liquid Density: Lighter than Water.
Volatiles vol % 52.6 Wgt% 43.5 Wgt per gallon: 8.14 Pounds.
Spec. Gravity: 0.97719

Appearance: AMBER LIQUID WITH SOLVENT ODOR
V.O.C.: 420 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOIGNITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSION RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
```

# Appendix C. MSDS for Water-Sr Paint parts A & B

Page: 1	MATERIAL SAFETY DATA SHEET Printed : 07/22/04 For Coatings, Resins and Related Materials Revised : 10/22/03								
	SECTION	I - PRODUCT INDI	ENTIFICATION						
	DEFT, INC. (CAGE 17451 VON KARMAN IRVINE 92614	AVENUE E	nformation Phone: mergency Phone: HEMTREC Phone:	(800) 424-9300					
Product Class Trade Name Product Code C.A.S. Number	: MIL-PRF-85582D, : 44GN072	1 x	dazard Ratings: none -> extreme 0> 4						
	SECTION	II - HAZARDOUS I	INGREDIENTS						

OSHA PEL Weight ACGIH Mm HG STEL Ingredients CAS # TLV STEL # TLV STEL PEL

2-2 26.520 100 ppm N.E. 100 ppm

2-8 0.010 50 ppm N.E. 50 ppm

-06-2 26.910 .001mg/M3 N.E. 1 mg/M3

4-40-3 0.830 .01 mg/M3 N.E. 1 mg/M3

3-67-7 4.600 10 mg/M3 N.E. 15 mg/M3

ACGIH/TLV & OSHA/PEL Exposure limits are for total dust. 78-92-2 98-82-8 7789-06-2 10294-40-3 13463-67-7 N.E. 12.5 6 68P N.E. N.E. N.E. N.E. sec-BUTYL ALCOHOL CUMENE STRONTIUM CHROMATE BARIUM CHROMATE TITANIUM DIOXIDE

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST. ALSO ANY UNLISTED INGREDIENTS.

#### N.E. = Not Established

SECTION III - PHYSICAL DATA Boiling Range: 211 - 306 Deg. F Vapor Density: Heavier than Air. Evap. Rate: 0.65 x n-Butyl Acetate Liquid Density: Heavier than Water. Volatiles vol \$ 43.0 Wgt \$ 26.8 Wgt per gallon: 10.80 Pounds. Spec. Gravity: 1.29652

Appearance: GREEN LIQUID WITH SOLVENT ODOR V.O.C.: 334

SOLUBILITY IN WATER: Insoluble PH: Not applicable AUTOIGNITION TEMPERATURE: No information found DECOMPOSITION TEMPERATURE: No information found CORROSION RATE: No information found VISCOSITY: Thin liquid to heavy viscous material MIXED VOC: 340 G/L OR LESS WHEN MIXED PER INSTRUCTIONS WITH 44GN072CAT.

MATERIAL SAPETY DATA SHEET Printed: 07/22/04
For Coatings, Resins and Related Materials
Revised: 10/22/03 Page: 1 R.
SECTION I - PRODUCT INDENTIFICATION IRVINE 92614 SECTION II - HAZARDOUS INGREDIENTS

| Meight ACGIH ACG OSHA PEL . STEL mm HG N.E. 16 6 68F N.E. 1 6 68F NITROETHANE 100 ppm N.E. ORGANOSILOXANE

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST. ALSO ANY UNLISTED INGREDIENTS.

#### N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 237 - 554 Deg. F Vapor Density: Heavier than Air.
Evap. Rate: 1.27 x n-Butyl Acetate Liquid Density: Heavier than Water.
Volatiles vol % 32.2 Wgt% 30.1 Wgt per gallon: 9.38 Pounds.
Spec. Gravity: 1.12605

Appearance: AMBER LIQUID WITH SOLVENT ODOR
V.O.C.: 345 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOTOMITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSION RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 44GN072 PER
INSTRUCTIONS.

# Appendix D. MSDS for Water-Ba Paint parts A & B

MATERIAL SAFETY DATA SHEET P: For Coatings, Resins and Related Materials Page: 1 Printed: 07/22/04 Revised : 10/27/03 SECTION I - PRODUCT INDENTIFICATION Manufacturer: DEFT, INC. (CAGE CODE 33461) 17451 VON KARMAN AVENUE Information Phone: (949) 474-0400 Emergency Phone: (800) 424-9300 CHEMTREC Phone: 800-424-9300 IRVINE 92614 CA ! Hazard Ratings: Health - 4 | Fire - 3 | 0 ---> 4 | Reactivity - 1 Product Class: TYPE I, CLASS C1, POLYAMIDE Trade Name : MIL-PRF-85582C(MIL-P85582B) Product Code : 44GN007 C.A.S. Number: NONE Personal Protection - G SECTION II - HAZARDOUS INGREDIENTS

		Weight		- Exposure	-	SHA	VP
Ingredients	Cas #	*	TLV	STEL	PEL	STEL	mm HG
2-BUTOXYETHANOL PETROLEUM NAPHTHA LT. AROMATIC 1,2,4 TRIMETHYLBENZENE CUMENE 1,3,5 TRIMETHYLBENZENE BARIUM CHROMATE ZINC CHROMATE	111-76-2 64742-95-6 95-63-6 98-82-8 108-67-8 10294-40-3 11103-86-9	13.230 4.730 4.950 0.250 1.360 23.090 0.020	25 ppm 100 ppm 25 ppm 50 ppm 123 mg/M3 .01 mg/M3	N.B. N.E. 35 ppm N.E. N.E. N.E.	25 ppm N.E. N.E. 50 ppm N.E. .1 mg/M3	N.E. N.E. N.E. N.E. N.E.	.9 & 7.7F 3 & 68F

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST. ALSO ANY UNLISTED INGREDIENTS.

#### N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 306 - 343 Deg. F Vagor Density: Heavier than Air.
Evap. Rate: 0.46 x n-Butyl Acetate Liquid Density: Heavier than Air.
Volatiles vol % 44.0 Wgt% 25.6 Wgt per gallon: 12.68 Pounds.
Appearance: GREEN LTQUID WITH SOLVENT ODOR
V.O.C.: 389 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOIGNITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSTON RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 44GN007CAT
PER INSTRUCTIONS.

MATERIAL SAPETY DATA SHEET Printed: 07/22/04 Page: 1 For Coatings, Resins and Related Materials SECTION I - PRODUCT INDENTIFICATION Manufacturer: DEFT; INC. (CAGE CODE 33461) 17451 VON KARMAN AVENUE 461) Information Phone: (949) 474-0400 Emergency Phone: (800) 424-9300 CHEMTREC Phone: 800-424-9300 CA IRVINE 92514 Product Class: TYPE I,CLASS C1,EPOXY | Hazard Ratings: Health - 3
Trade Name : MIL-PRF-85582C(MIL-P-85582B) | 0 ---> 4 Reactivity - 1
Product Code : 44GN007CAT | C.A.S. Number: NONE | SECTION II - HAZARDOUS INGREDIENTS Weight ACGIH O OSHA PEL STEL CAS # Ingredients 79-24-3 16.280 100 ppm N.E. 2530-83-8 0.610 N.E. N.E. 1 PPM TLV Suggested by DOW CHEMICAL. mm HG 100 ppm N.E. 16 & 68F N.E. N.E. 1 9 68F NITROETHANE ORGANOSILOXANE

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST. ALSO ANY UNLISTED INGREDIENTS.

#### N.E. = Not Established

SECTION III - PHYSICAL DATA

SECTION III - PHYSICAL DATA

Boiling Range: 237 + 554 Deg. F Vapor Density: Heavier than Air.
Evap. Rate: 1.27 x n-Butyl Acetate Liquid Density: Heavier than Water.
Volatiles vol % 17.8 Wgt% 16.3 Wgt per gallon: 9.53 Pounds.
Spec. Gravity: 1.14406

Appearance: AMBER Liquid With Solvent Odor
V.O.C.: 187 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOIGNITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSION RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
MIXED VCC: 340 G/L OR LESS WHEN MIXED WITH 44GN007
PER INSTRUCTIONS.

# Appendix E. Sample Data for % Cr⁺⁶ Calculation

This appendix includes the raw, uncorrected sample data used in calculating the percent dissociation of  $Cr^{+6}$ . Summarizing Chapter 3, petri dishes containing sanded particles in mucin were split into two fractions, and ultimately analyzed by ICP to determine the mass of  $Cr^{+6}$  per ml of mucin of each fraction analyzed. The calculations were accomplished in two steps. First, the concentration of  $Cr^{+6}$  of each fraction of the split sample was determined through ICP analysis. The ICP result was multiplied by the volume of each sample fraction analyzed:  $V_{T(to-ICP)}$  or  $V_{D(To-ICP)}$ . This provided the total mass of  $Cr^{+6}$  in the solution analyzed by ICP. Next, the volume of Dissolved ( $Cr_{OD}$ ) and Total ( $Cr_{OT}$ )  $Cr^{+6}$  from the initial samples were calculated. The mass of  $Cr^{+6}$  in each split fraction was divided by the initial volume of mucin used to make the solution:  $V_T$  ot  $V_D$ . These steps are illustrated by the equations below. The %  $Cr^{+6}$  dissociation was calculated by dividing  $Cr_{OD}$  by  $Cr_{OT}$ .

$$Cr_{OD} = \frac{ICP_D(ug/ml) * V_{D(To-ICP)}(ml)}{V_D(ml)}$$

Cr_{OD} mass dissolved Cr in initial sample per volume of mucin (ug/ml)

ICP_D Dissolved Cr ICP result (ug Cr/ml solute)

V_{D(To-ICP)} Volume of Dissolved Cr fraction (ml) analyzed by ICP

V_D Volume of Initial Dissolved Sample (ml)

$$Cr_{OT} = \frac{ICP_{T}(ug/ml) * V_{T(To-ICP)}(ml)}{V_{T}(ml)}$$

Cr_{OT} mass total Cr in initial sample per volume of mucin (ug/ml)

ICP_T Total Cr ICP result (ug Cr/ml solute)

V_{T(To-ICP)} Volume of Total Cr fraction (ml) analyzed by ICP

V_T Volume of initial Total sample (ml)

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	22.098	17.622	12.270		0.052	0.036	93%
	1	diss.		4.476		9.369	0.016	0.034	
	2	total	22.707	18.230	12.167		0.079	0.052	34%
Su		diss.		4.477		9.337	0.009	0.018	,
microns	3	total	22.244	18.384	12.220		0.121	0.081	59%
E	3	diss.		3.860		8.672	0.021	0.048	
1.1	4	total	22.179	17.679	12.190		0.046	0.032	66%
55 -		diss.		4.500		9.329	0.010	0.021	
0.6	5	total	22.844	18.452	12.335		0.108	0.072	52%
Particle size range 0.65	3	diss.		4.392		9.091	0.018	0.037	
ra	6	total	22.984	18.522	11.982		0.067	0.043	94%
size	0	diss.		4.462		9.257	0.020	0.041	
cle :	7	total	22.966	18.585	11.813		0.142	0.090	19%
ırti	, 	diss.		4.381		9.380	0.008	0.017	
Pa	8	total	22.988	19.224	11.628		0.540	0.327	89%
	O	diss.		3.764		8.734	0.126	0.292	
] ]	9	total	23.180	18.844	11.545		0.040	0.025	61%
	9	diss.		4.337		9.238	0.007	0.015	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	23.162	18.676	12.146		0.265	0.172	42%
,	1	diss.		4.486		9.324	0.034	0.072	
	2	total	22.347	17.868	12.242		0.118	0.081	93%
Su		diss.		4.479		9.383	0.036	0.075	
microns	3	total	21.709	17.204	12.087		0.106	0.074	102%
Ŭ.	3	diss.		4.505		9.232	0.037	0.076	
2.1	4	total	23.528	19.102	12.906		0.129	0.087	49%
		diss.		4.426		9.291	0.020	0.043	
e 1.1	5	total	22.507	18.070	12.265		0.157	0.107	54%
Particle size range	<u> </u>	diss.		4.437		9.133	0.028	0.057	
e ra	6	total	22.673	18.223	12.096		0.172	0.114	46%
siz		diss.		4.450		9.266	0.025	0.053	
cle	7	total	22.355	18.457	11.431		0.104	0.065	57%
arti	, 	diss.		3.897		8.918	0.016	0.037	
4	8	total	22.816	18.491	11.408		0.105	0.065	39%
		diss.		4.325		9.266	0.012	0.025	
	9	total	22.710	18.390	11.609		0.090	0.057	39%
	, J	diss.		4.320		9.208	0.010	0.022	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO} . ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	21.382	16.881	12.216		0.369	0.267	106%
	ı.	diss.		4.500		9.337	0.137	0.283	
	2	total	22.390	17.921	12.101		0.589	0.398	95%
Su	2	diss.		4.469		9.352	0.180	0.377	÷
3.3 microns	3	total	21.875	17.396	11.910		0.278	0.190	114%
Ĭ.	J	diss.		4.479		9.193	0.105	0.216	
3.3	4	total	23.222	18.843	12.302		0.152	0.099	79%
	4	diss.		4.379		9.228	0.037	0.079	
e 2.1	5	total	21.936	17.467	12.014		0.274	0.188	105%
Particle size range	<i></i>	diss.		4.469		9.192	0.096	0.198	
e ra	6	total	22.500	18.009	12.033		0.281	0.188	105%
siz	0	diss.		4.491		9.317	0.095	0.198	
cle	7	total	22.661	18.176	11.963		0.224	0.147	64%
arti	,	diss.		4.485		9.395	0.045	0.094	
P.	8	total	21.525	17.192	11.710		0.168	0.114	77%
	0	diss.		4.333		9.274	0.041	0.088	
	9	total	22.568	18.854	11.543		0.126	0.077	41%
	, , , , , , , , , , , , , , , , , , ,	diss.		3.715		8.721	0.014	0.032	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	22.436	17.967	13.620		2.117	1.605	110%
]	1	diss.		4.469		9.332	0.842	1.759	
	2	total	21.294	16.857	12.173		1.714	1.238	108%
<u>S</u>		diss.		4.437		9.291	0.639	1.338	
microns	3	total	21.138	16.747	12.596		1.410	1.060	107%
m;		diss.		4.391		9.132	0.547	1.139	
4.7	4	total	23.156	18.725	12.353		0.542	0.358	99%
		diss.		4.431		9.294	0.168	0.352	
e 3.3	5	total	21.828	17.469	12.223		0.812	0.568	103%
Particle size range	3	diss.		4.359		9.073	0.282	0.586	
e ra	6	total	22.859	18.334	12.292		1.461	0.980	102%
siz	0	diss.		4.525		9.363	0.482	0.997	
cle	7	total	22.983	18.392	11.703		0.844	0.537	84%
arti	′	diss.		4.592		9.477	0.218	0.450	
<u>a</u>	8	total	22.730	18.330	11.159		1.198	0.729	64%
	O	diss.		4.400		9.317	0.219	0.463	
	9	total	22.287	18.360	11.220		0.047	0.028	22%
	<i>y</i>	diss.		3.927		8.937	0.003	0.006	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	20.924	16.422	12.181		7.947	5.895	90%
	1	diss.		4.501	,	9.375	2.546	5.304	
	2	total	21.344	16.848	12.181		8.113	5.866	92%
y ₂		diss.		4.495	ŧ	9.387	2.594	5.416	
microns	3	total	22.023	17.548	12.020		5.973	4.091	102%
nic		diss.		4.475		9.207	2.022	4.160	
7	4	total	22.731	18.263	11.999		5.677	3.730	68%
4.7 -		diss.		4.468	·	9.358	1.219	2.553	
	- 5	total	22.418	18.130	12.162		7.037	4.721	93%
Particle size range		diss.		4.289		9.015	2.094	4.402	
Ze r	6	total	22.883	18.426	12.239		6.644	4.413	100%
e Si	0	diss.		4.457		9.287	2.109	4.395	
ticl	7	total	21.208	16.635	11.336		4.414	3.008	91%
)ar	,	diss.		4.573		9.476	1.322	2.740	
	8	total	20.903	16.584	11.785		4.102	2.915	97%
	· ·	diss.		4.319		9.233	1.323	2.828	
	9	total	21.512	17.262	11.149		2.624	1.695	97%
	<i>J</i>	diss.		4.250		9.094	0.767	1.642	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	20.235	15.816	12.021		68.935	52.393	26%
	1	diss.		4.419		9.262	6.467	13.555	,
	2	total	21.035	16.583	12.190		57.522	42.283	28%
,		diss.		4.451		9.344	5.712	11.990	
Su	3	total	21.287	16.816	12.070		41.751	29.968	36%
7+ microns		diss.		4.471		9.172	5.230	10.730	
	4	total	25.863	21.399	11.941		34.079	19.016	53%
	<b>T</b>	diss.		4.463		9.328	4.797	10.027	
Particle size range	5	total	21.660	17.251	12.112		72.017	50.563	28%
ra	J	diss.		4.409		9.088	6.770	13.955	
size	6	total	21.988	17.536	11.845		51.864	35.034	32% .
cle	0	diss.		4.452	,	9.265	5.459	11.360	
ırti	7	total	20.488	16.032	11.518	•	54.999	39.513	26%
Pa	,	diss.		4.456		9.362	4.938	10.375	
	8	total	20.918	16.397	11.839		34.654	25.021	35%
		diss.		4.521		9.366	4.285	8.878	
	9	total	21.394	17.030	11.662		24.024	16.451	45%
		diss.		4.363		9.187	3.497	7.364	

POLY-SR

			Initial		•	V _{D(TO-}	ICP _T	Cr _{OT}	
	Sample	Sample	Vol	$V_T$ or $V_D$	V _{T(To-ICP)}	ICP)	or	or CroD	% Cr
	#	type	(ml)	(ml)	(ml)	(mĺ)	$ICP_D$	(ug/ml)	dissociated
	1	total	21.344	16.882	11.865		0.197	0.138	118%
	.1	diss.		4.461		9.366	0.078	0.164	
	2	total	22.206	17.722	12.693		0.086	0.062	129%
		diss.		4.484		9.411	0.038	0.080	
	3	total	22.082	17.612	12.019		0.082	0.056	55%
	3	diss.		4.470		9.372	0.015	0.031	
	4	total	20.138	15.462	12.289		0.261	0.207	109%
	-	diss.		4.676		9.367	0.112	0.225	
	5	total	21.699	17.206	11.900		0.114	0.079	78%
Su		diss.		4.492		9.359	0.029	0.061	
icro	6	total	25.573	21.062	11.605		0.156	0.086	23%
Ē		diss.		4.511		9.408	0.010	0.020	
1.1	7	total	21.793	17.277	12.092		0.179	0.125	15%
55		diss.		4.516		9.345	0.009	0.019	
Particle size range 0.65 - 1.1 microns	8	total	21.806	17.340	11.478		0.440	0.291	6%
nge		diss.		4.466		9.313	0.009	0.018	
ra	9	total	22.578	18.038	12.116		0.113	0.076	23%
size		diss.		4.541		9.287	0.009	0.017	
cle	10	total	21.872	17.297	12.241		0.517	0.366	69%
ırti	10	diss.		4.575		8.905	0.129	0.252	
Pa	11	total	21.601	17.068	11.897		1.134	0.790	73%
	11	diss.		4.534		8.958	0.292	0.577	
	12	total	21.821	17.262	11.206		0.409	0.265	82%
	12	diss.		4.559		9.371	0.106	0.219	
	13	total	22.167	17.639	11.726		0.371	0.247	106%
	15	diss.		4.529		9.338	0.127	0.262	
	14	total	22.328	17,727	11.531		0.302	0.196	113%
	1.7	diss.		4.601		9.409	0.108	0.222	
	15	total	23.345	18.818	11.749		0.338	0.211	132%
		diss.		4.527		9.575	0.131	0.278	

POLY-SR

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	21.394	16.739	12.023		0.153	0.110	122%
	. I	diss.	,	4.654		9.556	0.066	0.135	
	2	total	21.193	16.642	12.117		0.166	0.121	125%
		diss.		4.551		9.490	0.072	0.150	
	3	total	22.809	18.372	12.119		0.138	0.091	62%
	J	diss.		4.437		9.338	0.027	0.056	
	4	total	20.652	16.225	12.496		0.347	0.267	103%
'		diss.		4.427		9.248	0.131	0.274	
	5	total	22.159	17.605	11.702		0.584	0.388	18%
Su	J	diss.		4.554		9.375	0.035	0.071	ì .
2.1 microns	6	total	21.587	17.165	11.731		0.124	0.085	54%
m i	0	diss.		4.422		9.139	0.022	0.046	
2.1	7	total	22.279	17.762	12.170		1.200	0.822	7%
		diss.		4.517		9.347	0.029	0.061	
e 1.	8	total	22.317	18.048	11.950		0.208	0.138	39%
Particle size range 1.1	6	diss.		4.269		9.151	0.025	0.053	
e re	9	total	22.758	18.032	11.598	·	0.166	0.107	16%
Siz		diss.		4.726		9.417	0.009	0.017	
cle	10	total	21.547	17.449	11.675		0.729	0.488	77%
arti	10	diss.		4.097		8.574	0.180	0.376	, 1
A.	11	total	21.881	17.470	11.921		0.692	0.472	86%
	11	diss.		4.411		8.845	0.203	0.408	
	12	total	22.033	17.547	11.731		0.425	0.284	96%
	12	diss.		4.486		9.177	0.133	0.272	
	13	total	22.333	17.857	12.155		0.495	0.337	104%
	13	diss.		4.476		9.316	0.169	0.352	
	14	total	22.066	17.537	11.615		0.500	0.331	109%
	17	diss.		4.530		9.391	0.174	0.361	·
	15	total	22.387	18.303	11.962		0.553	0.361	121%
	13	diss.		4.084		8.989	0.199	0.439	

POLY-SR

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	21.912	17.405	12.214		0.478	0.336	111%
	1	diss.		4.507		9.407	0.179	0.374	
	2	total	21.693	17.218	12.181		0.304	0.215	124%
		diss.		4.475		9.402	0.126	0.266	
	3	total	21.810	17.506	12.187		0.270	0.188	73%
		diss.		4.304		9.235	0.064	0.137	
	4	total	21.824	17.487	12.155		0.710	0.494	107%
		diss.		4.337		9.264	0.248	0.530	
	5	total	21.892	17.371	11.727		1.122	0.757	35%
Su		diss.		4.521		9.379	0.128	0.266	
CLO	6	total	16.117	11.485	12.059		0.563	0.591	20%
Ë		diss.		4.633		9.494	0.057	0.116	:
3.3 microns	7	total	22.135	17.592	12.063		0.476	0.327	54%
•		diss.		4.543		9.394	0.086	0.178	
Particle size range 2.1	8	total	21.987	17.484	12.087		0.455	0.315	47%
mg		diss.		4.503		9.350	0.071	0.147	
e ra	9	total	21.308	16.777	12.193		0.177	0.129	13%
siz		diss.		4.532		9.270	0.009	0.017	
icle	10	total	21.296	16.804	11.964	•	1.728	1.231	89%
art		diss.		4.492		8.949	0.547	1.089	
Ь	11	total	21.267	16.777	11.401		1.146	0.779	87%
	11	diss.		4.491		8.929	0.342	0.679	
.'	12	total	21.194	17.088	11.612		0.719	0.488	98%
		diss.		4.106		8.986	0.219	0.480	
	13	total	22.444	17.995	11.931		1.456	0.965	98%
		diss.		4.449		9.267	0.453	0.943	
	14	total	22.448	18.481	11.568		1.107	0.693	102%
	1.7	diss.		3.967		8.923	0.313	0.704	
	15	total	22.718	18.184	11.670		1.013	0.650	107%
		diss.		4.535		9.343	0.336	0.693	

POLY-SR

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	20.699	16.493	12.028		1.146	0.836	106%
	1	diss.		4.206		9.180	0.406	0.885	
	2	total	20.299	15.926	11.867		1.387	1.033	82%
		diss.		4.373		9.361	0.397	0.850	
	3	total	20.888	16.445	11.902		1.003	0.726	101%
	3	diss.		4.443		9.320	0.349	0.732	
	4	total	21.260	16.980	11.783		1.134	0.787	106%
	4	diss.		4.281		9.152	0.389	0.832	
	5	total	20.890	16.366	11.740		1.589	1.140	76%
Su	3	diss.		4.525		9.331	0.419	0.864	
- 4.7 microns	6	total	22.792	18.256	11.949		0.760	0.498	67%
mi		diss.		4.536		9.470	0.160	0.334	:
4.7	7	total	22.031	18.285	11.724		0.942	0.604	110%
	/ -	diss.		3.746		8.730	0.284	0.662	
Particle size range 3.3	8	total	21.192	16.775	11.704		1.430	0.998	69%
ıng	8	diss.		4.417		9.305	0.329	0.693	
13	9	total	20.117	15.606	12.097		0.514	0.398	23%
siz	9	diss.		4.511		9.272	0.045	0.093	
cle	10	total	21.664	17.129	11.751		3.744	2.568	90%
arti	10	diss.		4.536		8.958	1.171	2.312	
<u>a</u>	11	total	21.382	16.873	10.952		3.684	2.392	88%
	11	diss.		4.509		8.944	1.059	2.100	
	12	total	21.292	16.970	11.425		2.217	1.492	96%
	12	diss.		4.322		9.190	0.672	1.428	
	13	total	21.808	17.352	11.823		2.819	1.921	97%
	13	diss.		4.456		9.273	0.900	1.872	
	14	total	21.657	17.817	11.755		3.976	2.624	102%
	1.7	diss.		3.840		8.830	1.160	2.667	
	15	total	22.061	17.540	11.458		3.813	2.491	97%
		diss.		4.521		9.352	1.170	2.420	

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	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	18.279	13.995	12.015		4.214	3.618	97%
	1	diss.		4.284		9.249	1.633	3.526	
	2	total	19.706	15.305	11.991		3.888	3.046	93%
		diss.		4.400		9.328	1.343	2.846	
	3	total	19.945	15.492	11.974		3.103	2.399	101%
	3	diss.		4.453		9.328	1.154	2.417	
	4	total	19.672	15.237	12.023		2.707	2.136	103%
	4	diss.		4.436		9.326	1.048	2.204	
	. 5	total	19.655	15.166	11.890		5.471	4.289	47%
82	3	diss.		4.489		9.289	0.972	2.012	
7 microns	6	total	20.899	16.646	11.788		3.064	2.170	77%
nic	0	diss.		4.253		9.253	0.769	1.673	
7.	7	total	20.258	16.083	12.109		4.654	3.504	57%
7.		diss.		4.175		9.079	0.911	1.981	
Particle size range 4.7	8	total	20.897	16.425	11.564		4.212	2.965	58%
ang	0	diss.		4.472		9.361	0.818	1.712	
Ze I	9	total	16.112	11.644	12.191		1.187	1.243	55%
e Si	. ,	diss.		4.468		9.253	0.331	0.686	
tic	10	total	20.557	15.973	11.694		11.038	8.081	76%
ar	10	diss.		4.584		8.988	3.144	6.165	
	11	total	19.691	15.119	11.785		8.763	6.831	78%
		diss.		4.572		8.984	2.711	5.328	
	12	total	19.349	14.989	11.717		4.304	3.364	88%
	12	diss.		4.360		9.228	1.398	2.958	
	13	total	20.981	16.499	11.432		8.915	6.177	87%
	13	diss.		4.482		9.303	2.594	5.384	
	14	total	20.502	16.083	11.880		11.743	8.674	82%
	17	diss.		4.419		9.273	3.389	7.113	· .
	15	total	20.752	16.258	11.887		9.218	6.740	85%
L		diss.		4.494		9.370	2.762	5.758	·

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,	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	17.905	13.466	11.732		35.680	31.087	28%
		diss.		4.440		9.351	4.121	8.680	
	2	total	18.488	14.034	12.122		23.999	20.730	35%
	2	diss.		4.454		9.368	3.453	7.262	
	3	total	18.438	14.008	12.049		17.957	15.445	38%
	3	diss.		4.430		9.347	2.804	5.916	
	4	total	17.500	13.001	11.794		30.139	27.342	24%
	4	diss.		4.499		9.388	3.170	6.614	
	5	total	18.231	13.801	11.856		15.156	13.020	34%
	3	diss.		4.430		9.257	2.138	4.469	
Su	6	total	20.025	15.540	11.296	,	12.462	9.059	41%
CLO	0	diss.		4.486		9.397	1.779	3.726	
Particle size range 7+ microns	7	total	18.937	14.533	11.885		36.500	29.850	19%
7	7 -	diss.		4.404		9.248	2.746	5.765	
nge	Q	total	19.099	14.704	11.621		26.032	20.573	22%
la l	8 -	diss.		4.394		9.280	2.137	4.514	
size	9	total	12.334	7.900	11.823		13.536	20.257	19%
cle		diss.		4.434		9.207	1.856	3.853	
Ţ	10	total	20.313	15.718	11.810		48.433	36.390	35%
Pa	10	diss.		4.594		8.999	6.430	12.594	
	11	total	20.135	15.635	12.727		37.835	30.798	35%
	11	diss.		4.500		8.907	5.436	10.759	
	12	total	20.460	16.304	11.677		50.275	36.007	23%
	12	diss.		4.156		9.393	3.700	8.362	
	13	total	20.946	16.453	11.800		102.561	73.557	21%
] .	15	diss.		4.493		9,328	7.464	15.495	
	14	total	20.484	16.015	11.422		76.719	54.715	32%
		diss.		4.469		9.304	8.291	17.262	
	15	total	20.502	16.721	10.767		61.318	39.485	32%
	1.5	diss.		3.782		8.712	5.487	12.642	

			Initial			V _{D(TO-}	ICP _T	Crot	~ ~
	Sample	Sample	Vol	$V_T$ or $V_D$	V _{T(To-ICP)}	ICP)	or	or Cr _{OD}	% Cr
	#	type	(ml)	(ml)	(ml)	(ml)	ICP _D	(ug/ml)	dissociated
	1	total	20.584	16.460	11.549		0.186	0.131	21%
]		diss.		4.124		8.557	0.013	0.027	
	2	total	20.347	16.382	10.923		0.294	0.196	38%
		diss.		3.965		8.860	0.033	0.074	
	3	total	20.488	16.389	10.963		0.502	0.336	96%
	J	diss.		4.099		9.001	0.147	0.323	
	4	total	21.103	16.976	10.940		0.257	0.165	85%
	7	diss.		4.127		8.365	0.070	0.141	
	5	total	21.074	17.285	11.286		0.346	0.226	61%
	<i>J</i>	diss.		3.789		8.774	0.059	0.137	
	6	total	21.035	17.450	11.328		0.260	0.169	66%
		diss.		3.586	,	8.508	0.047	0.112	
Su	7	total	20.898	16.721	12.088		0.259	0.187	103%
- 1.1 microns		diss.		4.177		9.120	0.088	0.193	
	8	total	20.402	16.200	11.592		0.176	0.126	85%
1.1		diss.		4.202		9.294	0.048	0.107	
	9	total	22.334	18.305	11.573		0.237	0.150	91%
Particle size range 0.65		diss.		4.029		9.123	0.060	0.136	
uge	10	total	20.777	16.955	11.444		0.291	0.196	91%
ra	10	diss.		3.822		8.898	0.077	0.179	
size	11	total	20.848	16.723	11.173		0.252	0.169	100%
le s	11	diss.		4.125		9.368	0.074	0.168	
ırti	12	total	20.934	16.768	11.607		0.253	0.175	15%
Pa	12	diss.		4.166		9.370	0.011	0.026	
	13	total	25.114	20.989	12.379		0.234	0.138	19%
	13	diss.		4.125		9.400	0.011	0.026	
	14	total	21.330	17.283	11.984		0.179	0.124	30%
	14	diss.		4.047		9.287	0.016	0.037	
	15	total	20.221	16.160	12.045		0.135	0.100	52%
	13	diss.		4.061		8.984	0.024	0.052	
	16	total	20.398	16.313	11.998		0.178	0.131	40%
	10	diss.		4.086		9.374	0.023	0.052	,
	17	total	21.761	18.303	12.398		0.215	0.145	99%
	17	diss.		3.458		9.328	0.053	0.144	
	10	total	21.610	17.560	11.605		0.186	0.123	54%
	18	diss.		4.051		9.346	0.029	0.067	

	<b>1</b> ~ .		Initial			V _{D(TO-}	$ICP_T$	Cr _{OT}	
	Sample	Sample	Vol	$V_T$ or $V_D$	V _{T(To-ICP)}	ICP)	or	or CroD	% Cr
	#	type	(ml)	(ml)	(ml)	(ml)	ICP _D	(ug/ml)	dissociated
	1 1	total	21.240	17.168	11.412		0.311	0.207	62%
		diss.		4.072		8.544	0.061	0.129	
	2	total	21.110	17.557	11.467	-	0.328	0.214	84%
,		diss.		3.553	· · · · · · · · · · · · · · · · · · ·	8.440	0.075	0.179	
	3	total	21.049	17.081	11.217		0.822	0.539	77%
		diss.		3.968		8.865	0.186	0.416	
	4	total	21.108	16.923	11.018		0.428	0.279	86%
	4	diss.		4.184		8.459	0.118	0.239	
	5.	total	20.876	16.630	11.407		0.392	0.269	80%
	J.	diss.		4.246		9.100	0.100	0.214	
	6	total	21.207	17.038	11.460		0.336	0.226	88%
		diss.		4.169		9.117	0.091	0.200	
Su	7	total	20.384	16.177	11.198		0.442	0.306	103%
2.1 microns	/	diss.		4.207		9.149	0.145	0.316	
mic	8	total	20.363	16.204	11.762		0.354	0.257	112%
2.1	·	diss.		4.159		9.246	0.129	0.287	
•	9	total	20.732	16.780	11.664		0.420	0.292	101%
Particle size range 1.1		diss.		3.952		9.078	0.129	0.296	
Bu	10	total	21.393	17.197	11.915		0.353	0.244	101%
e ra	10	diss.		4.196		9.212	0.112	0.247	
siz	11	total	21.279	17.214	11.798		0.453	0.311	116%
cle	11	diss.		4.065		9.300	0.158	0.360	
arti	12	total	21.258	17.414	11.339		0.520	0.339	25%
<u>a</u> ;	12	diss.		3.844		9.102	0.036	0.084	
	13	total	20.432	16.300	11.998		0.291	0.214	36%
	13	diss.		4.132		9.392	0.034	0.077	
	14	total	20.534	16.426	11.931		0.291	0.211	43%
	14	diss.		4.108		9.328	0.040	0.092	
	15	total	20.442	16.438	12.017		0.307	0.225	27%
	15	diss.		4.004		9.258	0.026	0.060	
	16	total	21.077	17.024	12.271		0.292	0.210	58%
,	10	diss.		4.053		9.336	0.053	0.122	
	17	total	21.069	17.352	11.391		0.471	0.309	98%
		diss.		3.716		9.308	0.122	0.304	
	18	total	21.044	17.039	11.705		0.249	0.171	43%
	10	diss.		4.006		9.265	0.032	0.074	

	Sample #	Sample type	Initial Vol (ml))	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	21.146	16.936	11.318		0.686	0.458	92%
		diss.		4.210		8.694	0.203	0.420	,
	2	total	20.792	16.735	11.423		0.527	0.360	96%
		diss.		4.057		8.935	0.157	0.347	
	3	total	20.028	15.864	10.931		0.563	0.388	100%
		diss.		4.164		9.015	0.180	0.389	
	4	total	21.919	18.082	11.486		0.777	0.493	75%
	4	diss.		3.837		8.110	0.174	0.369	
	5	total	21.264	17.752	11.238		0.669	0.424	101%
	٦	diss.		3.513		8.471	0.178	0.429	
	6	total	20.659	16.471	10.842		0.610	0.401	84%
	0	diss.		4.188		9.110	0.156	0.339	
St	7	total	20.670	16.530	11.600		1.100	0.772	110%
3.3 microns	'.	diss.		4.140		9.102	0.385	0.846	
l j	8	total	19.924	15.783	11.332		0.725	0.521	102%
3.3		diss.		4.142		9.216	0.239	0.532	
	9	total	20.617	16.428	12.018		0.632	0.462	103%
Particle size range 2.1		diss.		4.189		9.316	0.214	0.476	
luge	10	total	21.568	17.361	12.092		1.066	0.743	107%
2 2	10	diss.		4.207		9.237	0.361	0.793	
size	11	total	20.643	16.448	11.201		0.691	0.471	97%
cle	11	diss.		4.195		9.377	0.204	0.455	
it	12	total	20.944	17.261	11.424		0.764	0.506	38%
P	12	diss.		3.684		8.919	0.078	0.190	
	13	total	20.766	16.589	12.029		0.624	0.452	27%
	. 13	diss.		4.177		9.380	0.055	0.123	
	14	total	20.570	16.935	12.141		0.478	0.343	35%
	14	diss.		3.634		8.927	0.049	0.121	
	15	total	20.329	16.220	11.487		0.425	0.301	46%
	13	diss.		4.109		9.329	0.062	0.140	` .
	16	total	20.771	16.701	12.548		0.526	0.395	47%
		diss.		4.070		9.350	0.080	0.184	
	17	total	21.277	17.242	12.275		0.732	0.521	110%
,	1/	diss.		4.035		9.247	0.251	0.574	
	18	total	20.953	16.895	11.496		0.389	0.265	28%
	10	diss.		4.059		9.321	0.032	0.074	

Sample   type   type   vol				Initial			V _{D(TO-}	ICP _T	Cr _{OT}	
Total   20.258   16.053   11.261   1.741   1.221   98%   diss.   4.205   8.665   0.581   1.198   1.07%   diss.   4.179   8.667   0.714   1.482   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.670   1.6		1 -		1	_	V _{T(To-ICP)}		_		
Total   20.546   16.367   11.036   2.055   1.385   107%		#	type		(ml)	(ml)	(ml)			dissociated
Company		1	total	20.258	16.053	11.261		1.741	1.221	98%
Section   10   10   10   10   10   10   10   1		1	diss.		4.205		8.665	0.581	1.198	
		2	total	20.546	16.367	11.036		2.055	1.385	107%
10   10   10   10   10   10   10   10		2	diss.	-	4.179		8.667	0.714	1.482	
Company		2	total	19.878	15.694	11.637		2.027	1.503	111%
		3	diss.		4.184		9.061	0.771	1.670	
Section   10   10   10   10   10   10   10   1		4	total	20.941	17.485	11.402		1.089	0.710	106%
Section   Color   Co		4	diss.		3.456		7.778	0.333	0.750	
		_	total	20.524	16.522	10.761		2.308	1.503	109%
Table   Content   Conten		3	diss.		4.002		8.232	0.798	1.641	
Table		6	total	21.181	17.088	11.891		2.169	1.509	110%
		0	diss.		4.094		9.041	0.751	1.658	1.1
10   total   21.044   16.804   12.111     2.071   1.492   108%	St	7	total	20.661	16.481	11.555		2.209	1.549	108%
10   total   21.044   16.804   12.111     2.071   1.492   108%		'	diss.		4.180		9.130	0.767	1.675	
10   total   21.044   16.804   12.111     2.071   1.492   108%	mi	o	total	20.374	16.285	11.746		2.745	1.980	108%
10   total   21.044   16.804   12.111     2.071   1.492   108%	4.7		diss.		4.089		8.998	0.969	2.133	
diss.   4.241   9.341   0.730   1.608     10	•	9	total	21.044	16.804	12.111		2.071	1.492	108%
13     total 21.090 16.914 11.809     1.416 0.988 46%       diss.     4.176     9.364 0.204 0.458       14     total 20.442 16.325 12.257 1.609 1.208 29%       diss.     4.116 9.318 0.153 0.346       15     total 19.848 16.486 12.061 1.374 1.005 28%	(n)		diss.	•	4.241		9.341	0.730	1.608	
13     total 21.090 16.914 11.809     1.416 0.988 46%       diss.     4.176     9.364 0.204 0.458       14     total 20.442 16.325 12.257 1.609 1.208 29%       diss.     4.116 9.318 0.153 0.346       15     total 19.848 16.486 12.061 1.374 1.005 28%	l nge	10	total	21.380	17.233	11.755		1.856	1.266	109%
13     total 21.090 16.914 11.809     1.416 0.988 46%       diss.     4.176     9.364 0.204 0.458       14     total 20.442 16.325 12.257 1.609 1.208 29%       diss.     4.116 9.318 0.153 0.346       15     total 19.848 16.486 12.061 1.374 1.005 28%	1.0	10	diss.		4.147		9.173	0.624	1.381	
13     total 21.090 16.914 11.809     1.416 0.988 46%       diss.     4.176     9.364 0.204 0.458       14     total 20.442 16.325 12.257 1.609 1.208 29%       diss.     4.116 9.318 0.153 0.346       15     total 19.848 16.486 12.061 1.374 1.005 28%	size	11	total	21.360	17.491	11.585		3.003	1.989	110%
13     total 21.090 16.914 11.809     1.416 0.988 46%       diss.     4.176     9.364 0.204 0.458       14     total 20.442 16.325 12.257 1.609 1.208 29%       diss.     4.116 9.318 0.153 0.346       15     total 19.848 16.486 12.061 1.374 1.005 28%	cle	11	diss.		3.869		8.923	0.953	2.197	
13     total 21.090 16.914 11.809     1.416 0.988 46%       diss.     4.176     9.364 0.204 0.458       14     total 20.442 16.325 12.257 1.609 1.208 29%       diss.     4.116 9.318 0.153 0.346       15     total 19.848 16.486 12.061 1.374 1.005 28%	arti	12	total	21.702	17.606	10.646		2.277	1.377	27%
diss.     4.176     9.364     0.204     0.458       14     total     20.442     16.325     12.257     1.609     1.208     29%       diss.     4.116     9.318     0.153     0.346       15     total     19.848     16.486     12.061     1.374     1.005     28%	P.	12	diss.		4.097		9.270	0.167	0.377	
diss.     4.176     9.364     0.204     0.458       14     total     20.442     16.325     12.257     1.609     1.208     29%       diss.     4.116     9.318     0.153     0.346       15     total     19.848     16.486     12.061     1.374     1.005     28%		12	total	21.090	16.914	11.809		1.416	0.988	46%
diss.     4.116     9.318     0.153     0.346       15     total     19.848     16.486     12.061     1.374     1.005     28%		13	diss.		4.176		9.364	0.204	0.458	
diss. 4.116 9.318 0.153 0.346 total 19.848 16.486 12.061 1.374 1.005 28%		1./	total	20.442	16.325	12.257		1.609	1.208	29%
		14	diss.		4.116		9.318	0.153	0.346	
		15	total	19.848	16.486	12.061		1.374	1.005	28%
diss. 3.361 8.658 0.109 0.282		13	diss.		3.361		8.658	0.109	0.282	
16 total 21.035 17.540 12.074 0.950 0.654 90%		16	total	21.035	17.540	12.074		0.950	0.654	90%
diss. 3.495 8.845 0.232 0.588		10	diss.		3.495		8.845	0.232	0.588	
17 total 21.054 17.521 12.333 2.089 1.470 66%	]	17	total	21.054	17.521	12.333		2.089	1.470	66%
diss. 3.533 8.825 0.386 0.965		1/	diss.		3.533		8.825	0.386	0.965	
18 total 20.902 16.889 12.249 0.852 0.618 39%		10	total	20.902	16.889	12.249		0.852	0.618	39%
diss. 4.013 9.233 0.105 0.242		10	diss.		4.013		9.233	0.105	0.242	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	19.780	15.611	11.174		9.087	6.504	96%
	1	diss.		4.170		8.641	3.025	6.270	
	2	total	19.553	15.546	11.080		7.668	5.465	103%
		diss.		4.007		8.518	2.646	5.625	
	3	total	20.230	17.078	10.943		5.454	3.495	106%
	3	diss.		3.152		8.094	1.439	3.695	
		total	20.649	16.528	10.779		6.009	3.919	107%
	4	diss.		4.121		8.359	2.067	4.192	
	5	total	19.888	15.709	11.178		9.086	6.466	101%
	)	diss.		4.180		8.410	3.252	6.544	
	6	total	21.308	17.115	11.215		6.623	4.340	112%
	0	diss.		4.192		9.100	2.229	4.839	,
S	7	total	20.359	16.140	11.782	-	6.647	4.852	106%
l O	/	diss.		4.218		9.152	2.365	5.131	
7 microns	8	total	19.195	15.058	11.851		14.405	11.337	90%
7 1		diss.		4.137		9.106	4.659	10.253	
7-	9	total	19.764	15.551	11.457		6.464	4.762	105%
Particle size range 4.7		diss.		4.213		9.327	2.261	5.006	
ang	10	total	20.774	16.653	10.869		4.078	2.661	121%
Ze r		diss.		4.121		9.161	1.447	3.217	
s siz	11	total	19.754	15.571	11.821	,	9.770	7.417	102%
ticle	11	diss.		4.183		9.250	3.418	7.558	
ar	12	total	20.615	16.601	11.495		4.432	3.069	69%
1		diss.		4.015		9.236	0.922	2.121	• •
	13	total	20.060	15.931	11.815		7.487	5.552	25%
		diss.		4.129		9.315	0.613	1.384	
	14	total	19.184	15.082	11.958		4.520	3.584	39%
	1-7	diss.		4.101		9.348	0.616	1.404	
	15	total	19.531	15.870	12.009		5.060	3.829	32%
	1.5	diss.	<u> </u>	3.661		8.936	0.498	1.215	
	16	total	20.858	16.815	12.017		4.053	2.896	66%
		diss.		4.043		9.316	0.830	1.914	
	17	total	20.052	16.072	12.158		8.638	6.535	97%
	1,	diss.		3.980		9.254	2.722	6.329	
	18	total	20.270	16.225	11.945		3.746	2.758	39%
		diss.		4.045		9.291	0.466	1.071	

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	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
		total	20.169	15.916	11.442		44.841	32.236	49%
,	1	diss.	20.107	4.253	11.772	8.755	7.730	15.912	4770
		total	20.404	16.592	11.406	0.755	43.451	29.870	59%
	2	diss.	20.404	3.812	11.400	8.278	8.177	17.759	3770
		total	19.993	15.791	11.354	0.270	29.970	21.549	67%
	3	diss.	17.775	4.202	11.554	9.029	6.762	14.530	0770
		total	20.734	16.540	11.322	7.027	26.559	18.181	69%
	4	diss.	20.734	4.195	11.522	8.496	6.182	12.519	0770
		total	19.595	15.444	11.642	0.470	41.469	31.260	53%
	5	diss.	19.393	4.152	11.042	8.403	8.220	16.637	3370
		total	20.987	16.890	10.886	6.403	35.327	22.769	59%
	6	diss.	20.967	4.097	10.000	9.031	6.068	13.377	3970
		total	20.218	15.981	11.689	9.031	35.173	25.727	62%
S	7	diss.	20.216	4.237	11.009	9.141	7.392	15.947	0270
G			19.980		11.411	9.141		54.044	38%
nic	8	total	19.960	15.785	11,411	0.157	74.761		36%
Particle size range 7+ microns	9	diss.	20.590	4.195 16.373	11.479	9.157	9.315 33.564	20.336	65%
ge 7		total	20.390		11.4/9	0.216	·····		03%
l ang		diss.	20.552	4.217	11 550	9.316	6.907	15.259	050/
Ze r	10	total	20.552	16.427	11.552	0.167	18.513	13.019	85%
e sir		diss.	10.040	4.125	11 (20	9.167	4.988	11.085	1 E 01
lick	11	total	19.848	15.676	11.628	0.220	58.973	43.744	45%
ar		diss.	20.700	4.171	11 (00	9.220	8.877	19.621	AE OI
	12	total	20.709	16.552	11.690	0.205	19.184	13.549	45%
		diss.	20.774	4.157	11.001	9.395	2.677	6.049	1107
	13	total	20.774	16.714	11.801	0.006	66.836	47.192	11%
		diss.	20.120	4.061	10 100	9.226	2.316	5.261	170
	14	total	20.130	16.007	12.122	0.041	38.507	29.161	17%
		diss.	20.404	4.123	10.000	9.341	2.247	5.092	100
	15	total	20.424	16.259	12.280	0.007	39.751	30.022	19%
	-	diss.	20.064	4.164	11071	9.387	2.530	5.702	0~
	16	total	20.064	16.024	11.951		87.265	65.083	9%
		diss.	10.011	4.040	10.00	9.324	2.589	5.974	000
	17	total	19.916	15.866	12.361	0.001	76.597	59.674	33%
		diss.	40.61.7	4.050	10.55	9.284	8.690	19.922	400
	18	total	19.815	15.821	12.078		61.007	46.572	10%
		diss.		3.994		9.287	2.094	4.869	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	21.078	16.872	11.636		0.197	0.136	60%
	1	diss.		4.206		9.316	0.037	0.081	
	2	total	20.922	16.754	11.680		0.157	0.109	74%
	2	diss.		4.168		9.518	0.036	0.081	
	3	total	20.795	16.575	11.766		0.244	0.173	70%
	3	diss.		4.220		9.373	0.054	0.121	·
	4	total	20.788	16.603	11.470		0.318	0.219	29%
	4	diss.	-	4.185		9.133	0.029	0.063	
	5	total	20.774	16.654	11.593		0.461	0.321	34%
		diss.		4.120		8.979	0.050	0.109	
	_	total	21.380	17.550	11.972		0.319	0.218	40%
	6	diss.		3.830		9.218	0.036	0.088	
us	7	total	20.954	16.858	11.803		0.380	0.266	85%
1.1 microns	'	diss.		4.097		9.116	0.101	0.226	
m.	8 -	total	21.339	17.113	12.029		0.461	0.324	76%
1.1		diss.		4.226		9.533	0.109	0.247	
	9	total	21.381	17.139	11.744		0.872	0.598	45%
0.6		diss.		4.242		9.527	0.119	0.266	
Particle size range 0.65	10	total	20.515	16.744	11.868		0.428	0.303	73%
rai	10	diss.		3.770		9.104	0.091	0.220	
ize	11	total	22.011	17.607	11.471		0.459	0.299	78%
le s	11	diss.		4.404		9.355	0.109	0.232	
rti	12	total	20.892	16.702	12.010		0.432	0.311	84%
Pa	12	diss.		4.190		9.489	0.116	0.262	
	13	total	19.939	16.197	12.064		4.223	3.146	39%
	15	diss.		3.742		9.107	0.507	1.234	
	14	total	20.069	16.188	11.841		0.559	0.409	37%
	14	diss.		3.881		8.917	0.066	0.152	
	15	total	20.351	16.720	12.089		0.466	0.337	32%
	13	diss.		3.632		8.985	0.043	0.106	
	16	total	21.531	17.468	11.990		0.307	0.211	13%
	10	diss.		4.063		9.373	0.012	0.028	
	17	total	21.619	17.776	11.863		0.293	0.195	22%
	1/	diss.		3.843		9.168	0.018	0.043	
	18	total	21.393	18.330	12.138		0.305	0.202	42%
	10	diss.		3.063		8.351	0.031	0.085	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	21.198	17.567	11.671		0.280	0.186	34%
	1	diss.		3.631		8.830	0.026	0.064	
	2	total	20.848	16.667	11.330		0.470	0.319	69%
	<u>L</u>	diss.		4.181		9.546	0.096	0.220	
	3	total	20.847	16.690	11.524		0.282	0.195	69%
		diss.		4.157		9.274	0.060	0.135	
	4	total	21.130	16.963	11.463		0.306	0.207	57%
	4	diss.		4.167		9.100	0.054	0.118	
	5	total	20.770	16.809	11.783		0.355	0.249	28%
1		diss.		3.961		9.172	0.030	0.069	
	6	total	20.869	16.921	11.339		0.216	0.145	64%
	0	diss.		3.948		9.331	0.039	0.093	
Su	7	total	21.230	17.005	11.629		0.607	0.415	58%
2.1 microns		diss.		4.225		9.527	0.107	0.242	
H H	8	total	21.519	17.268	11.717		0.590	0.400	66%
2.1	0	diss.		4.252		9.509	0.118	0.264	-
•	9	total	20.511	16.345	12.090		0.586	0.433	72%
Particle size range 1.1		diss.		4.166		9.476	0.138	0.314	
mg	10	total	21.032	16.806	11.859		0.631	0.445	65%
e ra	10	diss.		4.225		9.537	0.129	0.290	
siz	11	total	21.118	16.819	12.074		0.525	0.377	70%
cle	11	diss.		4.299		9.265	0.123	0.264	
arti	12	total	21.121	17.270	12.061		0.647	0.452	58%
A	12	diss.		3.851		9.149	0.111	0.264	
	13	total	20.895	16.795	11.848		1.270	0.896	7%
	15	diss.		4.100		9.438	0.028	0.065	
	14	total	20.141	16.106	12.325		0.720	0.551	16%
	17	diss.		4.035		9.069	0.040	0.090	
	15	total	20.662	17.077	11.632		0.935	0.637	11%
	13	diss.	í	3.586		8.928	0.029	0.072	
	16	total	21.834	17.769	11.759		6.244	4.132	4%
	10	diss.		4.065		9.383	0.068	0.156	
	17	total	20.831	16.768	12.106		0.983	0.710	16%
	1/	diss.		4.063		9.376	0.048	0.110	
	18	total	20.836	16.771	11.644		0.349	0.242	34%
	10	diss.		4.065		9.272	0.037	0.083	

			Initial			V	ICP _T	Cro- or	
	Sample	Sample	Vol	$V_T$ or $V_D$	V _{T(To-ICP)}	V _{D(TO-} ICP)	or	Cr _{OT} or Cr _{OD}	% Cr
	#	type	(ml)	(ml)	(ml)	(ml)	ICP _D	(ug/ml)	dissociated
	1	total	20.951	16.723	11.874		0.487	0.346	29%
		diss.		4.227		9.343	0.046	0.101	
	2	total	20.233	16.046	11.558		0.479	0.345	32%
		diss.		4.188		9.533	0.049	0.111	
	3	total	21.478	17.516	11.690		0.429	0.286	38%
		diss.		3.961		9.159	0.047	0.108	
	4	total	20.916	16.719	11.670		1.082	0.755	15%
		diss.		4.198		9.183	0.053	0.115	
	5	total	21.331	17.182	11.789		0.781	0.536	27%
		diss.		4.149		8.977	0.067	0.144	
	6	total	21.121	16.909	11.405		0.498	0.336	36%
	0	diss.		4.212		9.529	0.053	0.120	
Su	7	total	20.865	16.652	11.794		0.650	0.460	71%
3.3 microns		diss.		4.213		9.543	0.145	0.327	
Ĭ.	8	total	21.384	17.134	11.865		0.981	0.679	49%
3.3		diss.		4.250		9.573	0.146	0.330	
	9	total	21.080	16.848	11.938		0.920	0.652	40%
e 2.		diss.		4.233		9.522	0.116	0.261	
Particle size range 2.1	10	total	21.159	17.077	12.103		1.129	0.800	36%
e ra		diss.		4.082		9.416	0.123	0.284	
siz	11	total	21.362	17.200	11.669		0.883	0.599	46%
cle	11	diss.		4.161		9.169	0.124	0.273	
arti	12	total	20.443	16.214	12.071		0.821	0.611	44%
P.	12	diss.		4.229		9.519	0.118	0.266	
	13	total	20.200	16.103	11.930		2.719	2.014	9%
	13	diss.		4.097		9.452	0.081	0.187	
	14	total	20.579	16.485	12.255		1.029	0.765	10%
	17	diss.		4.094		9.108	0.035	0.079	
	15	total	20.507	16.469	12.064		9.924	7.270	16%
	13	diss.		4.038		9.336	0.515	1.191	
	16	total	20.747	16.643	12.088		7.766	5.640	3%
.	10	diss.		4.104		9.425	0.073	0.169	
	17	total	20.903	16.901	12.172	,	0.881	0.635	22%
		diss.		4.002		9.337	0.059	0.136	
	18	total	21.569	17.428	11.829		0.546	0.371	30%
	10	diss.		4.141		9.341	0.050	0.112	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	20.670	16.477	11.368		1.599	1.103	15%
		diss.		4.194		9.323	0.075	0.166	
	2	total	20.255	16.063	11.469		1.725	1.232	19%
		diss.		4.192		9.484	0.106	0.240	
	3	total	19.880	15.718	12.595		2.250	1.803	17%
		diss.		4.162		9.320	0.134	0.301	•
*	4	total	20.381	16.223	11.420		3.903	2.747	10%
	4	diss.		4.158		9.374	0.122	0.275	
	5	total	20.896	17.326	11.708		3.393	2.293	11%
	3	diss.		3.569		8.828	0.098	0.243	
	6	total	20.551	17.130	11.544		2.113	1.424	18%
	U	diss.		3.421		8.850	0.097	0.251	
Su	7	total	20.565	16.429	11.815	_	1.486	1.069	38%
4.7 microns		diss.		4.136		9.477	0.179	0.411	
H.	8	total	20.831	16.609	11.699		3.716	2.617	19%
4.7		diss.		4.222		9.533	0.223	0.503	
	9	total	21.071	17.099	11.851		3.124	2.165	23%
e 3.		diss.		3.971		9.271	0.209	0.488	
Particle size range 3.3	10	total	20.395	16.412	12.106		0.920	0.679	48%
e ra		diss.		3.983		9.289	0.139	0.323	
siz	11	total	20.772	16.622	12.146		2.493	1.822	20%
cle	11	diss.		4.151		9.153	0.164	0.362	
arti	12	total	21.111	16.816	12.013		1.012	0.723	36%
P.	12	diss.		4.295		9.605	0.118	0.263	
	13	total	20.332	16.827	12.084		6.258	4.494	8%
	15	diss.		3.505		8.878	0.147	0.373	
	14	total	19.411	15.344	11.966		4.533	3.535	9%
	17	diss.		4.067		9.079	0.147	0.327	
	15	total	20.842	16.800	12.409		3.490	2.578	12%
	1.5	diss.		4.042		9.345	0.134	0.310	
	16	total	20.999	16.905	12.241		9.717	7.036	5%
	10	diss.		4.095		9.409	0.139	0.319	
	17	total	21.067	16.980	11.868		3.016	2.108	12%
	17	diss.		4.087		9.391	0.110	0.253	
	18	total	21.523	17.468	11.636		1.481	0.987	15%
	10	diss.		4.055		9.296	0.066	0.151	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	19.729	15.543	11.576		6.897	5.137	10%
		diss.		4.186		9.285	0.221	0.490	
	2	total	20.237	16.057	11.714		3.351	2.445	13%
		diss.		4.180		9.483	0.137	0.312	
	3	total	20.237	16.070	11.670		10.492	7.619	8%
		diss.		4.167		9.347	0.279	0.626	
	4	total	19.988	15.831	11.745		12.822	9.512	7%
	4	diss.		4.157		9.084	0.288	0.628	
	5	total	20.548	16.401	11.718		8.194	5.854	8%
		diss.		4.147		9.377	0.206	0.465	
	6	total	20.491	16.344	11.692		9.826	7.029	6%
	0	diss.		4.147		9.468	0.176	0.402	
S	7	total	20.342	16.108	11.954		8.444	6.266	10%
Con	/	diss.		4.234		9.556	0.264	0.597	
nic	8	total	20.719	16.547	12.320		10.583	7.880	13%
- 7 microns		diss.		4.172		9.497	0.446	1.014	
	9	total	20.325	16.124	11.728		13.761	10.009	8%
Particle size range 4.7		diss.		4.201		9.498	0.337	0.762	
ang	10	total	20.722	16.632	11.525		4.322	2.995	14%
e r		diss.		4.089		9.390	0.178	0.409	
Siz	11	total	19.474	14.940	12.081		11.654	9.424	7%
icle	11	diss.		4.534		9.489	0.303	0.635	
ar	12	total	20.021	15.669	11.768		2.590	1.945	17%
	12	diss.		4.352		9.461	0.155	0.336	
	13	total	20.039	15.934	11.511		24.071	17.389	5%
	13	diss.		4.105		9.429	0.360	0.827	
	14	total	20.058	16.006	11.965		16.463	12.307	5%
	14	diss.		4.052		9.055	0.282	0.631	
	15	total	19.647	15.602	12.092		12.093	9.372	7%
	15	diss.		4.044		9.357	0.273	0.633	
	16	total	20.846	16.738	11.929		11.409	8.131	6%
		diss.		4.108		9.417	0.197	0.452	
	17	total	21.165	17.095	11.770		9.380	6.458	7%
	1/	diss.		4.070		9.370	0.206	0.474	
	10	total	20.401	16.329	12.135		4.175	3.103	11%
	18	diss.		4.072		9.250	0.153	0.347	

	Sample #	Sample type	Initial Vol (ml)	V _T or V _D (ml)	V _{T(To-ICP)} (ml)	V _{D(TO-} ICP) (ml)	ICP _T or ICP _D	Cr _{OT} or Cr _{OD} (ug/ml)	% Cr dissociated
	1	total	19.667	15.545	11.289		56.599	41.104	3%
		diss.		4.122		9.214	0.535	1.196	
	2	total	21.113	16.922	11.646		20.267	13.948	5%
		diss.		4.191		9.511	0.298	0.675	
	3	total	20.666	16.513	11.198		67.554	45.809	3%
	3	diss.		4.152		9.313	0.607	1.360	
	4	total	19.148	15.005	11.434		55.061	41.957	4%
	4	diss.		4.143		9.020	0.842	1.833	
	5	total	20.547	16.378	11.281		97.900	67.431	2%
	3	diss.		4.169		9.348	0.473	1.060	
	6	total	18.922	14.750	11.452		93.639	72.703	2%
	0	diss.		4.172		9.485	0.606	1.378	
	7	total	20.196	16.008	11.823		85.542	63.179	2%
ns	'	diss.		4.189		9.465	0.659	1.489	
CLO	8	total	19.998	15.757	12.033		80.627	61.574	2%
<b>.</b>		diss.		4.242		9.510	0.639	1.434	
7+	9	total	20.087	15.841	12.302	,	70.222	54.533	3%
nge		diss.		4.245		9.518	0.641	1.438	
Particle size range 7+ microns	10	total	19.789	15.649	11.433		78.424	57.294	2%
size	10	diss.		4.140		9.408	0.468	1.062	
cle	11	total	21.141	16.599	11.206		89.594	60.485	2%
ırti	11	diss.		4.542		9.493	0.557	1.164	
Pa	12	total	20.681	16.608	12.196		37.385	27.453	3%
	12	diss.		4.073		9.336	0.404	0.925	
	13	total	19.565	15.434	11.502		120.207	89.584	2%
	15	diss.		4.131		9.425	0.806	1.840	
	14	total	20.725	16.610	11.799		83.336	59.199	3%
	17	diss.		4.116		9.149	0.705	1.567	
	15	total	21.075	16.993	12.143		44.655	31.910	4%
	15	diss.		4.082		9.377	0.512	1.176	
	16	total	19.922	15.839	12.235		129.919	100.355	2%
	10	diss.		4.082		9.391	0.687	1.580	
	17	total	20.974	16.875	11.993		88.149	62.648	2%
	17	diss.		4.099	•	9.386	0.546	1.250	
	18	total	21.373	17.327	12.097		48.138	33.608	3%
	10	diss.		4.046		9.089	0.480	1.079	

# Appendix F. Cr⁺⁶ Dissociation Percentages

			+6 Dissociatio		·	
0.65 - 1.1	1.1 - 2.1	2.1 - 3.3	3.3 - 4.7	<b>4.</b> 7 - 7	7+ micron	
micron	micron	micron	micron	micron		
93%	42%	100%	100%	90%	26%	
34%	93%	95%	100%	92%	28%	
59%	100%	100%	100%	100%	36%	
66%	49%	79%	99%	68%	53%	
52%	54%	100%	100%	93%	28%	
94%	46%	100%	100%	99%	32%	
19%	57%	64%	84%	91%	26%	
89%	39%	77%	64%	97%	35%	
61%	39%	41%	22%	97%	45%	
		Doly Cn Cn+6	Dissociation			
0.65 - 1.1	1.1 - 2.1	2.1 - 3.3	3.3 - 4.7	4.7 - 7	1	
micron	micron	micron	micron	micron	7+ micron	
100%	100%	100%	100%	97%	28%	
100%	100%	100%	82%	93%	35%	
55%	62%	73%	100%	100%	38%	
100%	100%	100%	100%	100%	24%	
77077	100				2401	
78%	18%	35%	76%	47%	34%	
23%	18% 54%	35% 20%	76% 67%	47% 77%	41%	
	***************************************					
23%	54%	20%	67%	77%	41%	
23% 15%	54% 7%	20% 54%	67% 100%	77% 57%	41% 19%	
23% 15% 6%	54% 7% 39%	20% 54% 47%	67% 100% 69%	77% 57% 58%	41% 19% 22%	
23% 15% 6% 23%	54% 7% 39% 16%	20% 54% 47% 13%	67% 100% 69% 23%	77% 57% 58% 55%	41% 19% 22% 19%	
23% 15% 6% 23% 69%	54% 7% 39% 16% 77%	20% 54% 47% 13% 89%	67% 100% 69% 23% 90%	77% 57% 58% 55% 76%	41% 19% 22% 19% 35%	
23% 15% 6% 23% 69% 73%	54% 7% 39% 16% 77% 86%	20% 54% 47% 13% 89% 87%	67% 100% 69% 23% 90% 88%	77% 57% 58% 55% 76% 78%	41% 19% 22% 19% 35% 35%	
23% 15% 6% 23% 69% 73% 82%	54% 7% 39% 16% 77% 86% 96%	20% 54% 47% 13% 89% 87% 98%	67% 100% 69% 23% 90% 88% 96%	77% 57% 58% 55% 76% 78% 88%	41% 19% 22% 19% 35% 35% 23%	

Water-Sr Cr ⁺⁶ Dissociation								
0.65 - 1.1 micron	1.1 - 2.1 micron	2.1 - 3.3 micron	3.3 - 4.7 micron	4.7 - 7 micron	7+ micron			
20%	62%	92%	98%	96%	49%			
38%	83%	96%	100%	100%	59%			
96%	77%	100%	100%	100%	67%			
85%	86%	75%	100%	100%	69%			
61%	78%	100%	100%	100%	53%			
66%	88%	84%	100%	100%	59%			
100%	100%	100%	100%	100%	62%			
85%	100%	100%	100%	90%	38%			
91%	100%	100%	100%	100%	65%			
91%	100%	100%	100%	100%	85%			
99%	100%	97%	100%	100%	45%			
15%	25%	38%	27%	69%	45%			
19%	36%	27%	46%	25%	11%			
30%	43%	35%	29%	39%	17%			
52%	27%	46%	28%	32%	19%			
40%	58%	47%	90%	66%	9%			
99%	98%	100%	66%	97%	33%			
54%	43%	28%	39%	39%	10%			

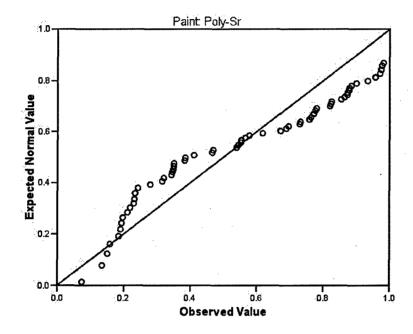
#### Water-Ba Cr⁺⁶ Dissociation 1.1 - 2.1 2.1 - 3.3 3.3 - 4.7 0.65 - 1.14.7 - 7 7+ micron micron micron micron micron micron 60% 34% 29% 15% 10% 3% 74% 69% 32% 19% 13% 5% 70% 69% 38% 17% 8% 3% 29% 57% 15% 10% 7% 4% 34% 28% 27% 11% 8% 2% 40% 64% 36% 18% 6% 2% 85% 58% 71% 38% 10% 2% 76% 66% 49% 19% 2% 13% 44% 72% 40% 22% 8% 3% 73% 35% 2% 65% 48% 14% 7% 78% 70% 45% 20% 2% 17% 84% 58% 43% 36% 3% 39% 7% 9% 8% 5% 2% 37% 16% 10% 9% 5% 3% 32% 11% 16% 12% 7% 4% 13% 2% 4% 3% 5% 6% 7% 22% 16% 21% 121% 2% 42% 34% 15% 30% 11% 3%

# **Appendix G. Summary of Mean Dissociation**

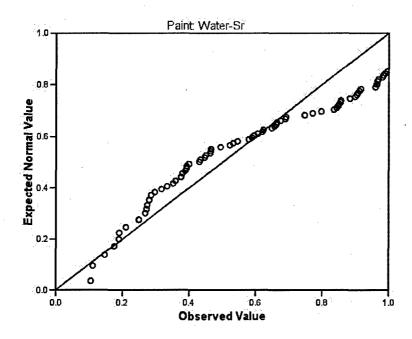
	Solvent-Sr		Poly-Sr		Water-Sr		Water-Ba	
	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev
0.65 - 1.1 micron	62%	26%	68%	35%	64%	31%	52%	23%
1.1 - 2.1 micron	58%	23%	70%	35%	73%	27%	44	25%
2.1 - 3.3 micron	84%	21%	74%	32%	76%	30%	31%	17%
3.3 - 4.7 micron	85%	27%	86%	20%	80%	30%	19%	11%
4.7 - 7 micron	92%	10%	79%	17%	81%	28%	9%	3%
7+ micron	34%	9%	29%	7%	44%	23%	3%	1%

# Appendix H. Normal Q-Q Plots

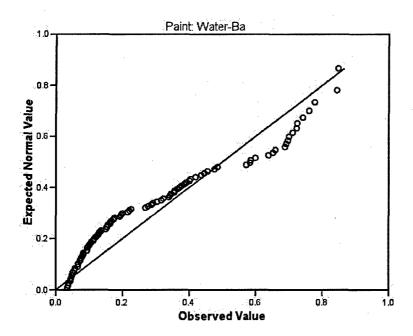
Normal Q-Q Plot of Percent Dissociation



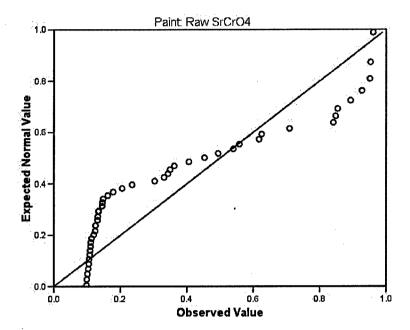
Normal Q-Q Plot of Percent Dissociation



Normal Q-Q Plot of Percent Dissociation



#### Normal Q-Q Plot of Percent Dissociation



#### Vita

Captain Steven Lange was born in Berlin, Vermont on September 17, 1972. He graduated from Lamoille Union High School in June 1991. He studied Civil Engineering at the University of Vermont where he graduated with a Bachelors of Science in 1997. After serving two years in the Vermont Air National Guard, he received a direct commission into the Air Force and entered active duty on Nov 2 1997.

His first assignment was at Altus AFB, OK where he served as a Bioenvironmental Engineer from 1997 until 1999. He then served as the Bioenvironmental Engineering Flight Commander from 1999 until 2001. He moved on to serve as the Installation Radiation Safety Officer and the Bioenvironmental Engineering Readiness Element Chief from 2001 to 2004 at Robins AFB, GA. In July 2004, he entered the Master of Science in Public Health graduate program at Uniformed Services University. Upon graduation in June 2006, he will be assigned to the Air Force Civil Engineering Support Agency, Tyndall AFB, Florida.